

DEVELOPMENT OF A CONVERGING WALL-JET INSTRUMENT
AND ITS USE TO MEASURE THE DYNAMIC RESPONSE
OF THE FLUORIDE ION-SELECTIVE ELECTRODE
TO FLUORIDE AND HALIDE INTERFERENT IONS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1996

Dedicated to the memory of my father, Forrey Balch Clay, and in memory of
Kirk Rutledge.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Vaneica Young, for the teaching and guidance she gave me while I was a graduate student. I would also like to thank my committee members for the great effort it takes to be on a student's dissertation committee. Your efforts are greatly appreciated.

No project like this could have been completed without the help of technical staff, and we are lucky to have very talented and knowledgeable technicians within the chemistry department. Carol Drum of the Marston Science Library helped me numerous times in finding literature references by on-line searches. The chemistry department electrical and machine shop technicians labored many hours on various aspects of the work presented herein. Without their expertise, advice, and labor, this project simply could not have been done. From the electronics shop, Russ Pierce has been instrumental in his technical advice relating to many of the electronic aspects of the converging wall-jet instrument. He designed much of the electronic circuitry used in our converging wall-jet instrument, built some of it, and filled in the gaps for everything else with his advice. Also from the electronics shop, Steve Miles helped me with some of the electronics related difficulties I faced in my last term of research. Our technical shop machinists have contributed with the design and fabrication of many parts of the converging wall-jet instrument as well.

Dailey Burch, Vernon Cook, Chester Eastman, and Joe Shalosky have been instrumental in taking my abstract ideas and translating them into real world functional components. They also taught me how to machine those components that I made and labored on those that I did not make myself. Equally important, they were called upon many times to fix broken parts and keep the instruments operational so I could keep the data coming in. I am indebted to all of these technical shop staff and give them my sincere thanks.

I could not have done this without the support of my family. The wisdom, advice, and love of my late father, Forrey Balch Clay, was largely responsible for me gathering the courage to go to graduate school and the will to succeed at it. My mother, Concetta Scalera Clay, also was a source of love, support, advice and wisdom. I have been truly blessed in having such wonderful, loving parents. They saw to it, through their own numerous and deep sacrifices, that four siblings and I had the chance to get a college degree, and for me to get two advanced degrees as well. My brother, Lonnie Clay, helped me through some tough financial times, and I greatly appreciate it.

I have been blessed with many wonderful friends through my years as a graduate student. Some friends who are former students at the University of Florida include Dr. Paul Sharpe and Dr. Rustom Kanga. We shared our trials, tribulations, and troubles as well as our friendship and fun. Other friends I met while at the university include Tony Aguilar, Wen Juan Cao, Richard Davies, Craig Hoag, Andrew Kehr, Conrad McCulley, and Yue Xu. And there are several friends I met

while at Knox College who still call me too late on Saturday nights: they are Dr. Paul Harris, Dr. Bob Bondurant, and Dr. Steve Briggs.

I would not have taken the first steps in getting a Ph.D. in chemistry if it were not for some teachers instilling an interest in the fascinating world of chemistry. Bruce Spencer, my high school chemistry instructor, is really the person who is most responsible for introducing me to the subject and inspiring me to study chemistry. He planted a seed in me, which was the desire to learn more and more about chemistry, and it is still alive within me. I thank him and my other teachers at Knox College and the University of Florida greatly for their efforts.

Lastly, I would like to thank Dr. Steve Hoke and the U.S. Army TACOM for financial support. However, the findings in this dissertation are not to be construed as an official Department of the Army position.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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By

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May, 1996

Chairperson: Dr. Vaneica Young
Major Department: Chemistry

Briefly, the dynamic response of an ion-selective electrode is the voltage response of the electrode following a rapid activity change of the primary and/or interferent ion(s) and is usually within the time domain of milliseconds to seconds. Experiments measuring the dynamic response of a fluoride ion-selective electrode to activity steps in fluoride, chloride/bromide, hydroxide, and chloride/bromide/hydroxide/cyanide are presented. An advanced converging wall-jet instrument capable of initiating activity steps within 7 milliseconds was built for this purpose and is described in detail. The dynamic response of a new fluoride ion-selective electrode for full scale voltage changes (t_{100}) has been measured and found to be 240 milliseconds to increasing (forward) decade steps in fluoride ion at

constant total ionic activity. Reverse (decreasing) activity steps showed a response time of 350 milliseconds. In both of these cases Nernstian voltage changes were seen. Decade steps in hydroxide ion, the only previously reported interferent species, resulted in complex dynamic voltage behavior. The voltage changes were sub-Nernstian and non-monotonic for both forward and reverse decade hydroxide activity steps. Surprisingly, large activity steps of chloride/bromide showed moderate non-monotonic voltage responses for increasing steps and small voltage responses for decreasing activity steps. The response time of the forward chloride/bromide activity steps was about 700 milliseconds and was much slower than when compared to the response to fluoride. The "four-ion" activity step consisted of an activity step of chloride, bromide, hydroxide, and cyanide simultaneously. The four-ion forward activity steps showed a dynamic response attributed in part to cyanide, while the reverse four-ion activity steps may have had a weak response due to cyanide. This research is one of the first efforts to measure the dynamic response of any ion-selective electrode in the presence of static case interferents, to show that non-interferents may give a dynamic voltage response, and to show that they may have response times differing greatly from the primary ion.

CHAPTER 1 INTRODUCTION TO THE DYNAMIC RESPONSE OF ION-SELECTIVE ELECTRODES

Definition of Dynamic Response and its Characterization

The static mode of operation of ion-selective electrodes. At one time or another, all chemists have used ion-selective electrodes to measure an analyte activity in a solution in a beaker. This mode of analysis is called the "dipping," "immersion," or "static" mode of operation.¹⁻³ With this familiar method, the reference and indicator electrodes are placed within a beaker of the analyte solution. The ion-selective electrode (ISE) is calibrated against a series of standard solutions. In the calibration of the ISE, it is often suggested that the ISE is cleaned, rinsed in a standard solution, then placed in the same standard while the operator waits until the electrode's potential has stabilized to within a few millivolts. The electrodes are then inserted in the analyte solution, again waiting for some minutes to pass while the potential stabilizes. The time evolution of the cell emf is shown in Figure 1-1. The dotted lines represent regions which are of no interest. The elapsed times $t_1 - t_2$ and $t_4 - t_5$ are stabilization times. The solid lines represent regions where the reading is made. In the manufacturer's operators manuals to

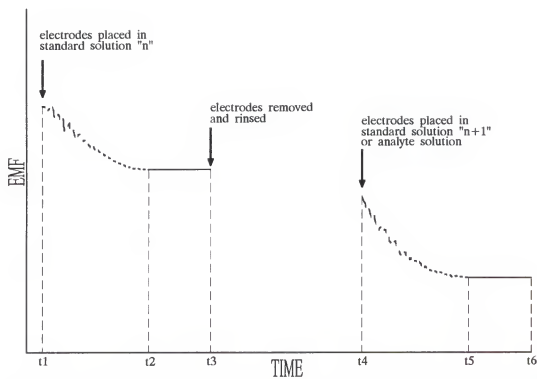


Figure 1-1. Typical dipping mode EMF versus time behavior for an ion-selective electrode.

ISEs, it has been suggested that stabilization times may last a few minutes duration.^{4,5}

The dynamic mode of operation of ion-selective electrodes and dynamic response. If one has the ability to change the activity of analyte solution very rapidly from an initial value in a first solution to a final value in a second solution, and the analyte containing solution is simultaneously flowed upon the indicator electrode, then a different time response behavior is seen. With reference to Figure 1-1, consider that we begin the procedure at t_2 and that at t_3 we switch the second solution onto the indicator electrode. The time evolution of the cell emf will be similar to that of $t_2 - t_6$, but with the region from t_3 to t_4 absent. A "stabilization time" as happens in the dipping mode of operation occurs, but the time scale is greatly lessened from the dipping mode of operation. We are interested in the response behavior represented by the dotted line. This time response behavior is known as the dynamic response of an ion-selective electrode. The method using such a setup is known as the dynamic mode of operation.^{1,2} To justify earlier statements, the fluoride ISE may require 1-2 minutes to stabilize in the static mode of operation, but in the dynamic mode of operation, the stabilization time is in the range of milliseconds.⁶ Thus the stabilization time for the case of an ISE used in the dynamic mode of operation is brief and is known as the response time of the ISE. While the response time of the ISE varies with several factors, such as electrode type,⁷⁻⁹ the magnitude of the change in activity,^{6,8} direction of the activity step change,^{6,8,9} et cetera, it is still useful as a figure of merit for an ISE.

Reasons why dynamic response is studied. Since the introduction of ISEs in the early part of this century, a continuing field of research interest has been the characterization of their dynamic properties. There are three reasons for this. First of all, the dynamic properties of ISEs have influenced the analytical methods for which they are used. Secondly, a curiosity about the mathematical form of the response behavior spawned methods for measuring the dynamic properties of ISEs. Thirdly, the mechanisms by which the electrodes respond can be elucidated by knowledge of their dynamic properties.

Dynamic response of the ion-selective electrode in the electrochemical cell.

The foremost method of measuring the dynamic response of an ion-selective electrode is the activity step method. In this method, a rapid change of analyte ion activity is created at the surface of the electrode membrane by a specially designed instrument. The overall transient response is the sum of three main contributions, shown in Figure 1-2. The first is the dynamic response of the electrode itself, and that is the quantity that we want to measure. The second contributing source is the measuring electronics, which in a well designed, modern instrument will contribute very minimally to the overall transient. This quantity can be measured by the use of a resistor in series with a square wave generator. If the output signal follows the input with less than a millisecond delay, then the electronics can be considered to be fast enough for measuring ISE dynamic response. The third and final contribution to the overall transient is the other sources within the electrochemical cell. Transient behavior sources here include the design of the electrochemical cell,

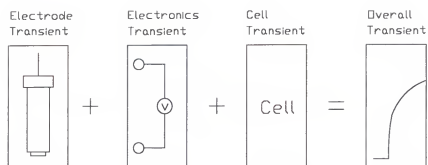


Figure 1-2. The sources of the overall transient signal when measuring an ion-selective electrode's response time.

the instrumental technique used to create the fast activity step, and the time dependence of other sources of potential in the cell such as diffusion and streaming potentials.^{1,2} As was previously mentioned, the transient characteristics of the electronics can be measured. Thus the measured transient can have this source subtracted away or otherwise compensated. Unfortunately, the resultant transient cannot have the contribution of the electrode and the cell distinguished from each other. There are three cases that arise. The first case is that the ISE response is extremely rapid with respect to the cell's response. In this case the transient signal obtained will be mostly due to the cell. The second case is where the contributions of the electrode and cell are roughly of the same time frame. The third case is for the electrode having a much slower response than the cell. In this case the activity step can be considered to be ideal and the measured signal can be said to be the response of the electrode itself. This is the desired situation for measurements of the electrode's dynamic response. Thus for a proper system to measure ISE dynamic response the electronics must be very rapid, the activity step creation must be very rapid, and other non-electrode time dependent sources of potential must be very rapid. It will be shown in Chapter 2 of this dissertation that the electronics and measuring setup used in the experiments presented herein are capable systems for measuring the dynamic response of the fastest responding ISEs yet reported in the literature.

Quantification of the response time of an ion-selective electrode. The transient function of an ion-selective electrode responding to its primary ion can be

described by a mathematical function. This mathematical function would include at least one time dependence or time constant. If the exact mathematical function is not known, then the response time can be used to characterize the electrode's performance. The response time is the amount of time after the creation of the activity step that it takes the electrode potential to reach a selected point. There are two definitions of response time suggested by the International Union of Pure and Applied Chemists (IUPAC).¹ The one used most commonly is t_α , where α is a percentage of the total voltage change of the electrode to its new equilibrium value after the activity step. Figure 1-3 illustrates the relationship between t_α , time, and potential. Figure 1-3 shows a simulated electrode dynamic response, with the change in voltage being 100 mV total. The data are for a plot of the function $E = 100 \text{ mV} * e^{(-t/\tau)}$. Elapsed time is given by t , e is the base of the natural logarithms, and E is the electrode's potential. The value of the time constant, τ , in Figure 1-3 is 0.1 seconds. Given the previous definition of t_α , if t_{50} is reported for an electrode, then the electrode will have changed half of the total change in potential after the activity step in the stated amount of time. For the data shown in Figure 1-3, the value of t_{50} is 0.07 seconds. Similarly, the value of t_{90} can be found to be 0.23 seconds. The values for t_{95} and t_{99} are 0.30 and 0.46 seconds respectively. The most commonly reported response times for t_α are where α is 50%, 90%, 95%, and 99% of the total voltage change. The second definition of response time is t' . This is defined to be the amount of time that has elapsed until the electrode has reached within 1 mV of its final equilibrium value. Figure 1-3 shows t' for the simulated

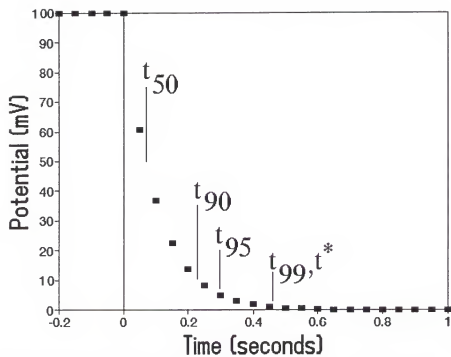


Figure 1-3. Plot of simulated dynamic response data for an anion ISE; various t_r response times are shown.

electrode response again, and the value of t^* coincides with the value of t_{99} , having a value of 0.46 seconds. The most appropriate definition of response time seems to be the former, t_a , since it does not vary with the valency of the ions being measured by the electrode.¹ The t_a method will be used to report response times in this dissertation. Values of response times in the millisecond time frame have been reported only for electrodes in specially constructed cells designed to create fast activity steps.⁶⁻¹⁴ There is no present definition of a response time when non-monotonic potential response is seen for an electrode responding to interferent ions.^{1,2}

Applications of Ion-selective Electrodes in Which Their Dynamic Response is of Importance

General Applications For Which the Dynamic Properties of Ion-selective Electrodes are Important

Ion-selective electrodes are often used as detectors in flowing streams, and in these applications, a knowledge of their dynamic response is of importance. It is fortunate that for most applications, the response time of the electrode is faster than the time frame of diffusion of analyte ions to the membrane.^{1,2} For applications where this is not true, then a distortion of the signal measured will take place due to slow electrode kinetics. This has often been noted for the sluggish enzyme electrodes.¹ Flowing stream applications would include all applications using ISEs as detectors for flow injection analysis.¹⁵⁻¹⁷ Other flowing stream applications are the monitoring of the reaction conditions in many industrial applications.^{1,4,5} Also,

their use as environmental monitors is forthcoming.^{4,5,18-20} Some clinical and physiological applications have been noted.^{1,4,5,21} In all of these applications, the response time of the electrode determines the sampling rate, the maximum attainable time resolution of the system being studied, or both.

Application Towards the Use of Ion-selective Electrodes in Portable Analyzers for Halon Fire Extinguisher Toxic By-products

The use of Halons in fire extinguishing and detection of hydrogen halide combustion products. Halon 1301 (bromotrifluoromethane) and Halon 1211 (bromochlorodifluoromethane) are gases used frequently in military vehicles as fire suppressants.^{22,23} These gases extinguish fires by a very interesting process--they engage in competitive reactions towards oxygen.²⁴ The Halon gases create free radical atomic halides by cleavage of the carbon-halide bond when heated. The halide free radicals react strongly and rapidly with oxygen, forming oxohalides, hydrogen halides, and molecular halides, amongst other combustion reaction products.²⁴ Thus the oxygen becomes less available for combustion reactions and the fire dies. Hydrogen halides are extremely toxic, and they will be formed whenever any Halon fire extinguishers are used to extinguish a fire.²⁵ Thus in a confined space, such as a vehicle, the use of a Halon fire extinguisher will solve the problem of the fire, yet possibly create the problem of a toxic atmosphere to breathe. Several United States national laboratories have investigated the toxicity of hydrogen halides and the extent of their production in fire suppression

environments. The United States Army has been involved in both types of studies. The determination of the levels of hydrogen halides in fire and post-fire environments where Halons have been used has proven difficult. These gases are extremely reactive, and the method of using evacuated vessels to hold atmosphere samples for subsequent wet chemical analysis has proven clumsy and imprecise.²⁶ Real time analysis has proven even more difficult. Infrared spectroscopy has been used with some success with burners, but manufacture of a portable instrument has not yet been possible.²⁵

The development of the Hoke analyzer for real time analysis of hydrogen halides in fire suppression studies. Dr. Steven F. Hoke of the United States Army Biomedical Research and Development Laboratories (USABRDL) has been interested in sampling fire suppression atmospheres for hydrogen halide content in real time. He has developed a portable instrument for the analysis of hydrogen chloride in fire environments. This instrument uses a chloride ion-selective electrode as the detector for hydrogen chloride. The atmosphere is pumped into an aqueous solution and then the stream is flowed over the electrode. The response of the chloride ion-selective electrode indicates the extent of chloride in the solution, which is related to the extent of hydrogen chloride in the sampled atmosphere. The Hoke monitor is easy to operate, relatively inexpensive, portable, and sensitive, but to date has been used only to monitor hydrogen chloride. From the previous discussion, hydrogen fluoride and hydrogen bromide may also be produced when a Halon fire extinguisher is used to combat a fire. Although not a

halogen halide, hydrogen cyanide, a hydrogen pseudohalide and another extremely toxic combustion product, is also produced in situations where fuel is present. The Hoke monitor in its present form is unable to measure the concentrations of hydrogen fluoride, hydrogen bromide, or hydrogen cyanide in the test atmospheres. Since this is of importance, it is desirable for the Hoke monitor to be modified to include these capabilities. To do so requires the addition of fluoride, bromide, and cyanide electrodes in the analyzer. However, these electrodes suffer from several halide interferences, and thus specificity is difficult to obtain for the analysis. A second problem is that the interferences can alter the surface composition of the electrode membranes, and thus can alter the response kinetics, a knowledge of which is crucial to the accuracy of analysis. In this dissertation, the results of basic research aimed at overcoming these two major impediments to the use of several electrodes to simultaneously monitor in real time the HF, HCl, HBr, and HCN produced in fire extinguisher tests are presented.

Non-static Case Problems Associated With Using Ion-selective Electrodes With Interferent Ions in Their Dynamic Mode of Operation

The two problems that interferences cause in the dynamic mode of operation of ISEs. There are two main problems that are introduced when using ion-selective electrodes in their dynamic mode of operation when dealing with solutions containing interferent ions. The first problem is that the response to the primary ion and to the interfering ion can be of substantially different time frames.^{1,27-30} Figure

1-4 illustrates this problem. The figure shows the response of an anion ISE when a primary ion and an interferent ion are together in the same solution. The overall lineshape is an exponential composed of two separate exponentials, one for each ion. The voltage changes are 59 mV for each ion. The response to the primary ion is rapid ($\tau = 0.1$ sec) and its contribution to the electrode voltage change is almost complete within 1 second after the change in solution. However, the electrode voltage slowly changes over 10 seconds. It is evident that the asymptotic region is actually due to the response to the interferent ion ($\tau = 1$ sec), but since the voltage is so slowly changing, the effect could easily be mistaken for electrode drift. The second problem is that the surface of the membrane can change upon exposure to the interferent ion, contaminating the surface, and leading to vastly different response kinetics.^{1,27,28,30} Figure 1-5, Figure 1-6, and Figure 1-7 together illustrate this problem. A new membrane and a graph of its dynamic response is shown in Figure 1-5. The membrane is composed of a binary salt of composition AB. The response of the new membrane to its primary ion is relatively fast ($\tau = 0.1$ sec). In Figure 1-6, we see the same membrane and its dynamic response to its primary ion after the membrane has been contaminated with an interferent ion, "C." The chemical composition at the surface of the membrane is now $AB_{0.5}C_{0.5}$. The dynamic response has been affected by the contamination as well, because the response is much slower ($\tau = 1$ sec) than for the new membrane shown in Figure 1-5. Figure 1-7 shows the membrane and dynamic response after cleaning the surface free of contamination. The chemical composition of the membrane is now

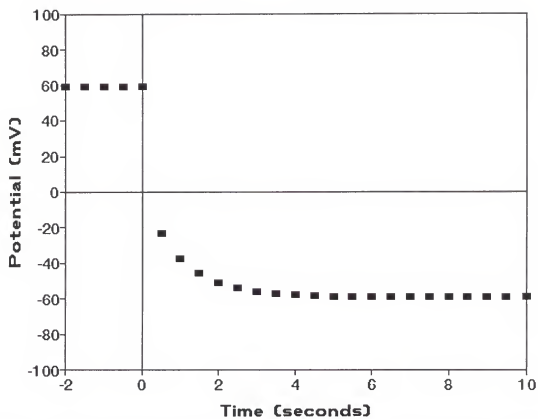
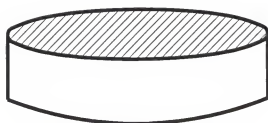


Figure 1-4. Response of an ISE to a two ion solution. The response to one ion is much faster than the other ion.



AB

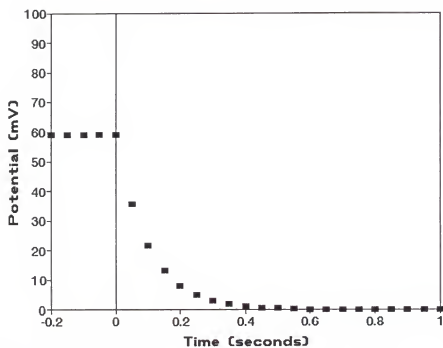


Figure 1-5. Fast response of a new membrane of composition AB.

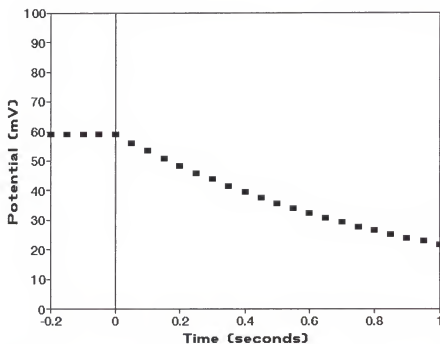
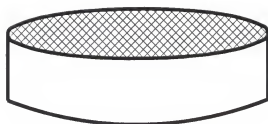


Figure 1-6. Slow response of a contaminated membrane. Species "C" is the contaminant. Compare the much faster response for the same solution in Figure 1-5.

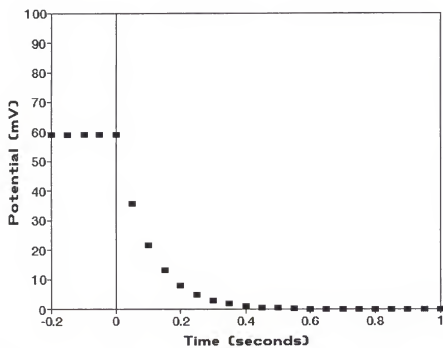
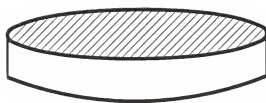


Figure 1-7. Fast response of a recovered membrane. This membrane is the membrane in Figure 1-6 after polishing or chemical etching.

AB, the same as the new membrane. The membrane surface has been recovered by either polishing or chemical etching and the membrane is now thinner. The recovered membrane's dynamic response has returned to the same level of performance as for the new membrane. The first problem can possibly be overcome by measurement of the dynamic properties of the primary and interferent ions and through the use of chemometric approaches to the data analysis. The second problem is overcome in the static mode of operation by the polishing of the membrane, bringing the surface to its original chemical and physical state. For dynamic mode applications, the polishing of the electrode may interrupt the on-line monitoring of the reaction, effluent, et cetera, and thus is not a very convenient solution to the problem. Also the electrode itself may be imbedded within machinery and be very difficult to reach. We have investigated in our lab the use of chemical etching to remove the contaminated layer of the membrane, exposing a surface corresponding to the original uncontaminated surface. For some electrodes, this should be a solution to the second problem.

Nonuniform Response Kinetics Towards Primary and Interferent Ions

The electrode will show a dynamic response to both the primary and interferent ion if the activity of the interferent is large enough. The selectivity in the dynamic mode of operation will not necessarily follow the selectivity in the static mode of operation.^{1,27-30} The response towards the interferent ion may or may not cause non-monotonic behavior. In all cases where non-monotonic behavior is seen,

the response kinetics are nonuniform. Figure 1-8 shows the resultant non-monotonic dynamic response lineshape for an ISE responding to its primary ion and an interferent ion. The electrode rapidly changes potential in response to the interferent, and ΔE_1 shows the potential overshoot to the interferent ion. This region is due to the kinetically favored interferent ion diffusing towards the surface of the membrane in preference to the primary ion. The interferent species adsorbs onto the membrane surface, while the primary ion in the membrane desorbs into the stagnant layer. The second region shows that thermodynamic equilibrium is re-established, with a relaxation to a steady state amount of interferent having replaced the primary ion at the membrane surface. This relaxation leads to a steady state overall potential change, ΔE_2 . The behavior is due to the slower diffusion of the primary ion through the stagnant layer into the bulk solution, until all equilibria are re-established. Note that the surface will now be contaminated to some extent with the interferent ion. The potential behavior is non-monotonic because of the initial decrease, and subsequent increase in potential of the ISE. This part of the curve is for a "forward" activity step of interferent, that is to say an increasing activity of interferent. The "reverse" step case is the opposite, decreasing activity of interferent. Upon a reverse activity step another potential overshoot is seen, and the potential change for this event is ΔE_3 . This would correspond to the rapid desorption and diffusion through the stagnant layer of the interferent into the bulk solution. The relaxation process is caused by diffusion of the primary ion through the stagnant layer and adsorption back to the membrane

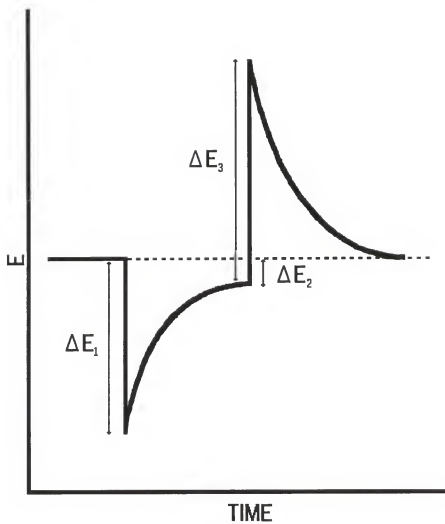


Figure 1-8. Non-monotonic dynamic response behavior of an ISE in the presence of an interferent ion.

surface. There have been equations that have attempted to describe the overall function of potential versus time for this case.^{1,27,30} In the case where monotonic behavior is seen, there still is the possibility that the kinetics towards the primary and interferent ions may differ largely. This means that the response of the slower ion may not be seen in its entirety or at all. This type of behavior was shown in Figure 1-4. More sophisticated chemometric approaches to the data analysis may provide for some measure of the activity of the slower responding ion. It has been suggested that the derivative of the dynamic response may show peaks corresponding to both ions. The height of the peaks in the derivative of the dynamic response may lead to quantitative information on both species.

The Possible Change in the Surface Composition of Ion-selective Electrodes as a Result of Exposure to Interferent Ions

The effect of the chemical composition of the ISE membrane on its dynamic response. The surface of an ISE membrane is in a state of continuous change as it is subjected to different analyte ion and interferent ion containing solutions. The response mechanism of all ISEs is in part due to the surface state of the ISE membrane,¹ and the surface state can effect the dynamic response as well.^{1,28,31} The surface of the membrane is affected by ion exchange, dissolution, and precipitation processes of primary and interferent ions taking place between the bulk solution and the ISE membrane surface, among other processes.^{1,27-30} Ions in the membrane dissolve into the bulk of the solution, and ions in the bulk of the solution

may precipitate back onto the surface of the membrane. It has been shown that solid state ISEs respond more slowly in the range of the limit of detection of primary analyte.³² This may be due to longer equilibration times for the dissolution of the membrane into the bulk solution. In the case of interferent ions, ion exchange processes are also taking place between primary and interferent ions in the processes of dissolution and adsorption. As a result of such contamination processes the chemical composition of the surface of the membrane may be changed, and this may affect the ISE static and dynamic response. Examples of other processes that change both the chemical composition of the membrane and dynamic response characteristics include pre-conditioning,^{1,28} leaching or etching,¹ and method of preparation.¹

The effect of the physical properties of the surface of an ISE on its dynamic response. In addition to chemical composition, physical properties of the membranes may effect the dynamic response. The surface morphology may change the physical properties which may in turn affect the dynamic response of the ISE. Previous studies have shown that the physical state of the membrane can effect electrode response in the dynamic or static modes. Homogeneity of the membrane, grain size, grain boundaries and cracks in the membrane were shown to effect AC impedance studies of membranes.¹ Surface resistance has a similar impact on the properties of the AC impedance spectra. When the surfaces of membranes are covered by highly resistive layers, as in the case of the hydrolyzed surfaces of glass membrane electrodes, the impedance spectra are greatly

affected.¹ Upon removal of the hydrolyzed surface layer the spectra changes to a state of lesser impedance.¹

The change in surface composition of ISE membranes as a result of exposure to interferents and the resultant changes in dynamic response. Since the exposure of the ISE membrane to interferent ions may result in a change of the chemical composition of the surface and/or bulk of the ISE membrane, the dynamic response of the ISE may be affected. A change in the chemical composition of the membrane can affect the static response of the ISE by changing its limit of detection, sensitivity, or selectivity. The dynamic response properties of the membrane may be altered as well. Figure 1-5, Figure 1-6, and Figure 1-7 showed this effect for a hypothetical membrane. As the surface of the membrane is changed in its chemical composition, the response time towards the primary ion may change. The performance of the ISE may degrade upon repeated exposure to the interferent ion. Likewise, the response time towards the interferent ion may change as the membrane is repeatedly exposed to the interferent ion. The use of chemical etching to renew the surface of the ISE membrane may be a solution to the problem in some cases, as is polishing the surface of the membrane. Both of these solutions seek to bring about a surface that is identical to the original surface in chemical composition, thus reversing what would be the long duration change in the chemical composition of the surface. Non-monotonic behavior has been seen in the dynamic response of ISEs to interferent ions in the so called "two-ion" range.^{27,28} Figure 1-8 showed the typical dynamic response line shape. The

non-monotonic behavior is thought to be a result of different kinetics for the rate of dissolution and precipitation, et cetera, for the primary and interfering ions.^{1,27-30} It is seen only in short time duration behavior. The effect is seen as potential overshoots brought about by kinetic factors, then relaxations due to thermodynamic considerations. These kinetic factors manifest themselves as a temporary non-equilibrium surface state for the membrane, which brings about the vastly different dynamic response characteristics. When thermodynamic equilibrium has been reached, the system behaves as one would expect with regard to its static characteristics, such as potential change. Hysteresis may or may not be preserved.

CHAPTER 2

INSTRUMENTATION AND METHODS USED TO MEASURE THE DYNAMIC RESPONSE OF ION-SELECTIVE ELECTRODES

In Chapter 1 the definitions of static and dynamic response of ISEs were given. It was noted that the static mode of operation is the much more commonly used method. Examples of simulated dynamic response potential versus time curves for ISEs were also shown. It was also mentioned that methods used to measure ISE dynamic response involved the rapid change of activity of primary and/or interferent ion(s) at the surface of the ISE membrane. This chapter will elaborate on the methods used to measure ISE dynamic response and will give details on the instruments used to accomplish the same.

With the activity step method, the potential of the indicator electrode is monitored after a rapid change in analyte ion activity and plotted as a function of time.^{1,2} The change in analyte activity should be as instantaneous as possible, resulting in a step function which looks like that shown in part a of Figure 2-1. The measured ISE response with an ideal instrument is shown in part b of Figure 2-1. Figure 2-1 shows the forward (increasing) activity step, while Figure 2-2 shows the reverse (decreasing) activity step. The directions of the potential change are opposite in direction for the forward and reverse steps, but the direction with respect to the activity step change is arbitrary. The reader is reminded that some electrodes

increase their potential upon an increase in analyte activity while some electrodes decrease their potential with an increase in primary ion activity. The moment of activity step creation is noted by t_0 . The ideality of the step change in analyte activity is a function of the design of the experimental apparatus used to create the activity step as well as the experimental conditions used. For example, if the flow rate of a wall-jet instrument is low, then the activity step may be of long enough duration to distort the measured dynamic response of the ISE.^{1,2} If, however, the flow rate of the wall-jet is increased, then the activity step creation will be rapid enough to allow for the undistorted dynamic response of the ISE to be measured. The design of the apparatus, however, will determine the lower limit of response time for ISEs that can be measured without distortion due to the nonideality of the activity step creation itself.^{1,2} One should be aware that in using the activity step method, the overall transient response measured will be a function of several individual contributing factors. These factors include the electronics used to measure the transient signal, the setup used to create the activity step, the experimental conditions selected for the instrument used to create the activity step, other time dependent sources of potential related to the electrochemical cell, and the dynamic response of the ISE itself.¹ For useful measurements of ISE response times, the sum of all of the aforementioned contributing factors (except the dynamic response of the ISE) should be much less than the dynamic response of the ISE itself.

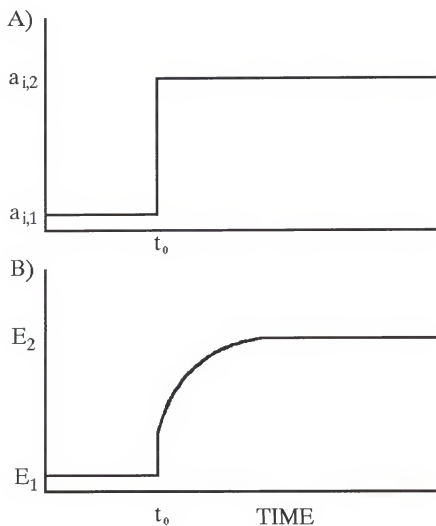


Figure 2-1. Potential versus time following a fast forward step change in activity. A) activity versus time curve B) potential versus time curve

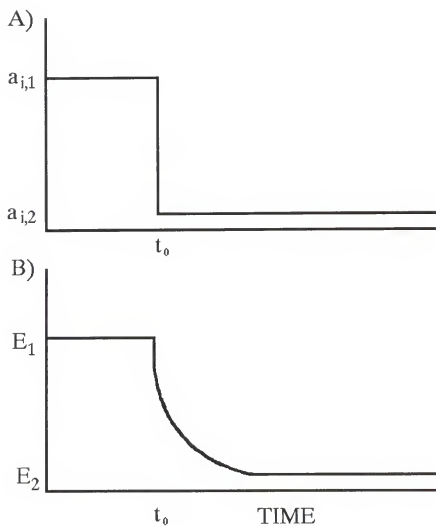


Figure 2-2. Potential versus time following a fast reverse step change in activity. A) activity versus time curve B) potential versus time curve

The Static Mode of Operation Used to Measure the Dynamic Response of Ion-selective Electrodes

The Dipping Method

The static response method applied to ISE dynamic response measurements. The "dipping" or static mode of operation of ISEs is commonplace and easily accomplished.^{1,2} The potential versus time response typical for this method was shown in Figure 1-1. This is by far the least complicated type of experiment that will reveal time response behavior of ISEs and uses the least technically advanced instrumentation. It also can lead to time response behavior that is greatly overestimated. The instrumentation typically consists of an indicator electrode, a reference electrode, two or more beakers containing unique solutions in each, an ion-meter, and a strip-chart recorder.¹ The electrodes are calibrated in their usual manner. After that, the time response behavior can be measured for the indicator electrode. To do so, the electrodes would be placed in the first beaker of solution and the strip-chart recorder pen set onto the paper. Once the potential has stabilized to a reasonable level, the paper feed would be switched on. The electrodes would then be removed from the beaker containing the first solution, and quickly placed into the beaker containing the second solution.^{1,2} For this reason, this method is also known as the immersion method.^{1,2} The second solution would have either a higher or a lower activity of analyte ion, and the potential of the electrode would change accordingly. The potential change would not be

instantaneous but would require a stabilization time. The zero of time would be considered to be the moment of insertion of the electrodes into the second beaker. The stabilization time would be reported as the response time of the electrode. The advantages to this method are that the method is familiar and the instrumentation is simple, so much so that this type of experiment can be done in most labs that have ISEs. Unfortunately, there are two main disadvantages to this method. The first and foremost disadvantage is that quite often the electrode's true dynamic response is not measured, but rather the electrochemical cell's transient response is measured. This method does not create a very ideal, instantaneous change in analyte ion activity at the surface of the ISE membrane. Unless the electrode's dynamic response is extremely slow, a serious distortion of the electrode's true dynamic response will be measured due to the nonideal, slow creation of the activity step. Secondly, the electrical continuity of the electrochemical cell is disrupted when the electrodes are removed from the first solution beaker and placed in the second solution beaker.^{1,2} Upon removal of the electrodes from the first solution, a charge will accumulate on the membranes' surface and their surrounding double layer, which can change the measured potential greatly. Again referring to Figure 1-1, we can see this effect by noting that the potential has changed from the time (t_3) when the electrodes were removed and rinsed until the time (t_4) that they were inserted into the second solution. The change in potential here is not due to the changing analyte activity, as the membrane is not yet sensing the new analyte solution, but is due to the capacitive charge buildup. This capacitive charge will

discharge upon insertion of the electrodes into the second beaker of solution, but the time to reach a steady state with reference to this charging may be a long duration compared to the dynamic response that we are trying to measure. The last major disadvantage of this method is the use of the strip-chart recorder to measure the transient signal, which can lead to distortions of the dynamic response of the electrode due to the relatively large time constant of the strip-chart recorder. It should also be said that the time constant for most strip-chart recorders is quite large in comparison to more suitable measuring electronics such as memory oscilloscopes and digital acquisition boards. The value of any "dynamic response" data using the static response method must be seriously questioned due to the major limitations of the method.

Methods Used to Create Fast Activity Steps for the Measurement of Ion-selective Electrode Dynamic Response

The Injection Method

The use of syringe mixing techniques (the "injection" method) to produce fast activity steps. This method involves the mixing of two solutions to produce the activity step.^{1,2} The first solution is placed in a beaker and is very rapidly stirred. The electrodes are immersed in the first solution. The potential is monitored until a stable plateau is reached. Then the second solution is introduced by fast injection into the stirred solution. The zero of time is considered to be the moment of injection of the second solution. Upon mixing of solutions one and two, a new solution of unique activity of primary ion is obtained and thus the activity step is

created. For forward steps in activity, the injected solution is a few milliliters of highly concentrated solution of the studied ion species. In this case, upon mixing of solutions one and two the new solution in the beaker will have a higher activity of primary ion. This results in a forward activity step. Effective reverse activity steps are not possible for this method. The electronics and the rest of the instrumentation are typically nearly the same as the static response method. There are advantages and disadvantages to the use of this method for dynamic response measurements. The first advantage is that, in comparison to the static response measurements, the electrical continuity is never broken. Thus there are no electrical charging effects noted for the injection method. In this respect it is superior to the static response method. There are two main disadvantages. First of all, the activity step creation is neither very rapid nor very reproducible. The hydrodynamic conditions (stirring rate, volume and rate of injection of solution, geometry of containing vessel, electrode position in the solution) are extremely difficult to control precisely.¹ Thus the amount of time needed to create the activity step will vary greatly. The time of initialization of the activity step will also vary. A second problem is that the time needed to mix the two solutions into a third solution of unique activity is often long enough to distort any measured electrode dynamic response.¹ Overall, this method should be considered comparable to the capabilities of the static response method in measuring electrode dynamic response. That is to say the usefulness of any information obtained in using this method is questionable. There are methods that

are far superior in their resolving power to reveal the true dynamic response behavior of ISEs. These are the specialized methods.

Specialized Methods Used to Create Fast Activity Steps

We have seen that the two previously mentioned methods for the measurement of electrode dynamic response fall short of desirable goals in their capabilities. The creation of activity steps by these methods result in activity steps whose time frame is certainly less than ideal, amongst other serious problems. In the last two decades, many special instruments have been built solely for the purpose of measuring ISE dynamic response characteristics. They create activity steps rapidly and reproducibly. Although every instrument that has been reported has unique features, I have classified them into four basic types. The four categories of instruments are in situ flow-cells, ex situ flow-cells, ex situ nonflow-cells, and in situ nonflow-cells. All use the general principles of the activity step method. There are two key defining criteria to distinguish the instrument types. The first criterion is where the activity step is created. If it is created at the surface of the membrane, then I call the technique in situ. If it is created somewhere else, probably in a tubing line, and then flowed onto the surface of the membrane, then I call the technique ex situ. The second criterion is whether a flow-cell or a streaming jet or jets of solution is used. The flow-cell techniques of course fall into the flow-cell category, while the streaming jet methods fall into the nonflow-cell category.

In situ flow-cells. In situ flow-cells have not yet appeared in the literature, but the design of an instrument that meets the criterion is possible. The defining features are the use of a flow-cell and the creation of the activity step at the site of the membrane. While the first criterion is met quite commonly in many instruments, the in situ creation of the activity step has been limited to wall-jet instruments thus far. An instrument of this type would use a flow-cell to hold the flow of solution, but at the same time use some means to create the activity step within the flow-cell. Such an instrument could look like the one shown in Figure 2-3. The flow-cell is a thin cavity in which the face of both electrodes can be mounted. An outlet line allows for the removal of the solution inside the flow-cell to a waste collector. Two separate lines into the flow-cell can be seen. The first and second analyte containing solutions are alternately flowed through their own separate lines into the flow-cell. The moment that the second solution is allowed to flow, the first solution is shut off. The flow of the second solution through the flow-cell rinses the remaining amount of the first solution through the outlet line, and in this manner the activity step is created at the surface of the membrane. The rest of the instrument would consist of solution reservoirs, a method to switch the solution flow on and off, electronics used to capture the transient signal, the electrodes, and the ion meter. The electronics used would need to be fast, therefore an oscilloscope or a digital acquisition board would be necessary. There are several advantages and disadvantages of this method. Compared to the previously mentioned techniques, a well designed in situ flow-cell would offer a more rapid and reproducible activity

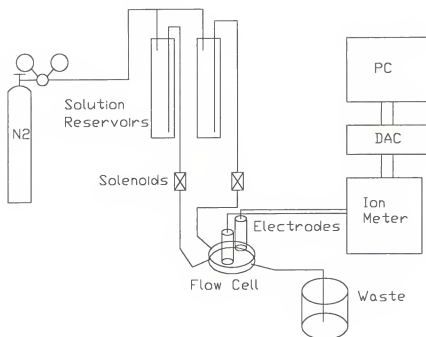


Figure 2-3. In situ flow-cell instrument for ISE dynamic response measurements.

step. Since the electrical continuity would be maintained throughout, no electrical charging would be expected, unlike the static method. The advantage of an in situ creation of the activity step could mean a sharper step function, due to the fact that the necessary mixing takes place near the surface of the membrane. The disadvantage of the method is also the probable lack of sharpness of the activity step due to the use of a flow-cell. It will take a finite time to rinse away the remaining portions of the first solution by the second. The time to accomplish this will probably be shorter than the two previously mentioned techniques, but will probably be longer than some of the techniques mentioned later in this chapter.

Ex situ flow-cells. This type of instrument was the first to gain wide use in the measurement of the dynamic response of ISEs. Flow injection analysis is a form of this type of instrument. Rechnitz and co-workers published three papers using ex situ flow-cells.^{12,13,33} The principle of activity step creation is the following. The first solution is allowed to flow into the flow-cell. The flow rates used are quite rapid. The potential is allowed to stabilize, and then the second solution is allowed to flow while the flow of the first solution is cut. This creates an activity step where the intersection of the first and second solution lines occurs. The intersection of the two lines may be a mixing chamber or a "Y" or "T" shaped connector. The continued flow of the second solution will push the activity step down the line until it enters the flow cell. At this point the potential change will begin to occur. The schematic of such an instrument is shown in Figure 2-4. Note that the setup is very similar to the in situ flow-cell, with the previously mentioned changes. The biggest difference

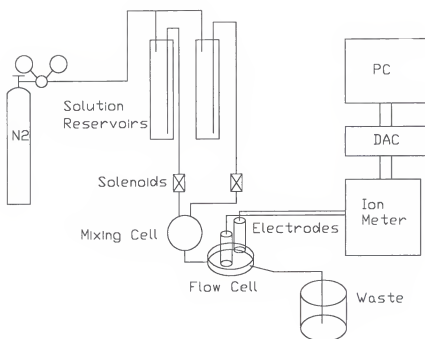


Figure 2-4. Ex situ flow-cell instrument for ISE dynamic response measurements.

between this setup and the in situ flow-cell method is the connection of the two solution lines before they reach the flow cell. The instrument has two main disadvantages, the first of which is the use of the mixing chamber. There will be a finite amount of time needed to rinse the first solution away by the second. This means that the step function will not have a nearly infinite initial slope at the point of activity step creation. The resulting activity step therefore will be nonideal. Secondly, there will be a significant time delay between when the two solutions mix together and when they reach the ISE. This amount of time will be very much a function of the solution viscosity, the flow rate of solutions, and other factors. This delay time can be compensated for if and only if the trial to trial reproducibility is excellent. I do not believe the former to be very probable, because of the many factors which will influence the amount of delay time between solution mixing and ISE wetting. Since both a mixing chamber and flow-cell are used, two sources of rinsing related nonideal activity step creation are present. The in situ flow-cell should show superior performance because only one source of rinsing related nonideal behavior is present. The advantage of the ex situ flow-cell should be the more reliable and rapid creation of activity steps than either the dipping or injection methods. The operating principles are otherwise like that used in the in situ flow-cell instrument, and the rest of the instrument comprises similar components.

Ex situ nonflow-cells (fixed wall-jet instruments). The only instrument of this type that has appeared in the literature thus far was demonstrated by Pungor and co-workers.³⁴ Their results for this type of instrument were not as good as for the

class of instrument described in the next paragraph. In this instrument a flow-cell is not used but rather a more open configuration is used. The instrumentation is shown in Figure 2-5. Two reservoirs holding two different solutions are pressurized with nitrogen gas. These reservoirs have tubing lines leading into them, which are the nitrogen gas inlet lines. There are also tubing lines which are outlets for the stream of pressurized solution. The stream is controlled by means of two independent electromagnetic valves. Further down the solution lines and after the point of the valves the two lines are connected to each other by a "Y" connector of tubing. The system allows the two streams to be alternately and independently flowed through their lines and through the "Y" connector. The third short piece of tubing acts as nozzle to direct the wall-jet to the surface of the membrane. Because the activity step is created at the intersection of the three pieces of tubing in the "Y" connector, and not at the surface of the membrane, the method must be considered to be *ex situ*. The disadvantage of the method is that the activity step is not created at the surface of the ISE membrane. This means that there will be some delay time between the instant that the activity step is created and the moment when the activity step reaches the surface of the ISE. Also, this quantity of time is likely to show a larger degree of trial to trial variance than the *in situ* nonflow-cell type of instruments. Further, there will inevitably be some undesirable mixing of the two solutions together at the "Y" junction. This means that the activity step created will have a less than infinite rising slope and be less than ideal. The advantage of the method is that the amount of mixing induced nonidealities are probably less than

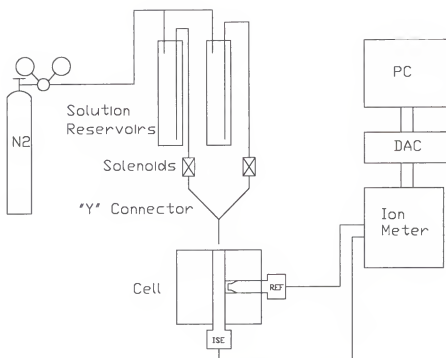


Figure 2-5. Ex situ nonflow-cell (fixed wall-jet) instrument for ISE dynamic response measurements.

for both of the flow-cell methods. The activity step with this method is likely to be created in a shorter amount of time, more ideally, and more reproducibly, than for either of the two flow-cell techniques. Thus it is likely that the performance of this type of instrument is superior to both flow-cell techniques. While Pungor and co-workers showed good results with this type of instrument,³⁴ their switched wall-jet instrument performance was far superior.^{10,11,35,36}

In situ nonflow-cells (switched and converging wall-jet instruments). Although the performance of the previously mentioned special methods are superior to the static and injection methods, their performance is probably not as good as the switched and converging wall-jet methods. Unfortunately, most instruments have not been well characterized, so one can speak of these methods as being the best only in theory. Few authors have actually made more than one instrument, and usually very little information about performance has been quantified, so it is difficult to compare the performance of instruments beyond stating that one method will outperform another in theory. However, based on the reports that have been made on instrument design and performance, it is very likely that these two methods are the best for measuring the dynamic response of ISEs. Both the switched wall-jet method of Pungor and co-workers^{10,11,35,36} and the converging wall-jet method of this author use individual streams of unique solutions sprayed upon the surface of the electrode membrane. The activity step of both methods is created in situ, rapidly, and reproducibly.

The wall-jet method in general. The switched wall-jet instrument of Pungor and co-workers^{10,11,35,36} was a successor to the fixed wall-jet instrument which was shown in Figure 2-5. If one can use two separate lines carrying unique solutions and alternately spray them onto the surface of the membrane (the generalized wall-jet method) then two main advantages will be realized. First of all, the delay time that was present in the ex situ methods will be minimized for the wall-jet methods, because the activity step is created at the surface of the membrane. Since a flow-cell is not used, then there is no time needed to flush away the first solution by the second within the flow-cell for the wall-jet methods. The advantage of the wall-jet method lies in the simple way that the activity step is created. There are only a few events that take place to create activity steps with this method. The first of which is the switching of the second solution on while the first is shut off. The second event is for the stream of the second solution to reach the membrane. The third event of the general wall-jet method is for the second solution to completely cover the ISE membrane. The fourth event is the rinsing away of the first solution stagnant layer by the second solution. No other major events are necessary to create an activity step. These events are necessary in all of the special methods, but the other special methods include additional steps that probably take a great deal of time. The few events taking place in wall-jet methods, and the fact that the events are rapid, is the key to the success of the method. However, it requires a slightly more sophisticated instrument to create alternating wall-jet streams of analyte containing solution flowed onto the surface of the ISE membrane.

The switched wall-jet method. Pungor and co-workers have developed two different switched wall-jet instruments. These instruments are very similar in principle of operation. The second instrument held both the indicator and reference electrodes in a cell so as to maintain electrical continuity between them.^{10,11} The earlier instrument did not have a cell to hold the electrodes, but rather the junction of the reference electrode was held against the indicator electrode's membrane.^{28,32,35-37} The result was that the spill-over of the solution being sprayed onto the membrane contacted the junction of the reference electrode and provided for the electrical continuity of the two electrodes with each other. While this method showed very good performance, Pungor and co-workers eventually developed the second instrument which used a cell and gave even better performance. A diagram of their second instrument is shown in Figure 2-6. Two reservoirs of unique solutions under nitrogen pressure are continuously flowing onto the electrochemical cell. The electrochemical cell holds both the indicator and reference electrodes which send the signal to the ion meter, analog to digital converter (ADC), and personal computer. The first solution is flowed directly onto the middle of the ISE membrane. Simultaneously, the second solution flows onto a drain in the cell and goes to a waste collector (not shown). A moveable bar holds both of the wall-jet nozzles parallel but separate from each other. At the moment that the activity step is to be initiated, a solenoid valve is opened by a signal. This allows the air driven piston to move the bar holding the two wall jets to the right. The bar is allowed to move until it hits a stop, and ends in a position such that the second solution is

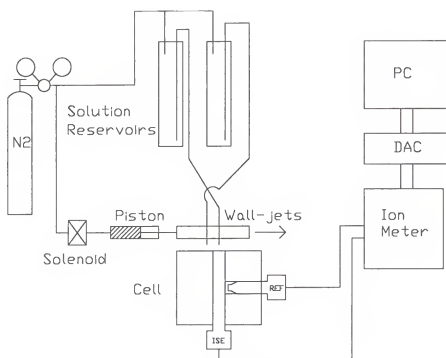


Figure 2-6. In situ non flow-cell (switched wall-jet) instrument for ISE dynamic response measurements.

flowing onto the center of the membrane. Simultaneously the first solution is now flowing through a drain to a waste collector. The activity step has been initialized when the first instances of the second solution reach the ISE membrane, and is finished when the last traces of the first solution are washed away from the indicator electrode. For the reverse activity step, a second solenoid (not shown) is opened and allows the air to drive a second air piston that is placed on the other end of the sliding block holding the two wall-jets (not shown). Pungor and his co-workers claimed that their best switching times were 7 ms, using an optical arrangement to measure the position of the sliding block.¹¹ However, they were able to measure the time of travel of the block to an accuracy of only ± 2 ms.¹¹ Undoubtedly their method led to the creation of very fast activity steps. But the quantity that they measured was the time needed to move the block, not the time needed to create an activity step. The reason for this is that the block may move very quickly, but if the flowing streams are too slow, the solutions will lag behind the movement of the block and take a finite amount of time to catch up once the block has finished moving. One can think of trying to hit two different objects with a stream of water from a garden hose. The person is hitting the first object with the stream, and then begins to move the hose. The nozzle eventually points directly at the second object, when the person quits moving the hose. But at this moment, the stream will not yet hit the second object. A short time later (the lag time) the stream will hit the second object. Remembering that there are four events taking place for the wall-jet activity step to take place, Pungor and his co-workers have measured only the first

step of the activity step process, the switching time. The time needed for the second solution to reach the membrane (the lag time) and cover the membrane completely were not measured. It may be that with a very high linear flow rate that the latter two quantities are very small, on the order of a few milliseconds, but Pungor and his co-workers did not demonstrate this. The last step, rinsing away the stagnant layer of the first solution by the second solution, would be a very difficult quantity to measure indeed. Overall, the switched wall-jet offers very good performance levels. The simplicity of the technique should allow for a very fast, reproducible, and in situ creation of the activity step. It has significant advantages of reproducibility over all of the previously mentioned techniques. It has all of the advantages of the in situ creation of the activity step. But the design that I have created and the resulting instrument offer some advantages over the switched wall-jet instrument, and its performance has been well characterized.

The Design, Fabrication, Theory, and Characterization of the Converging Wall-jet Instrument

Experimental Section

Introduction to the converging wall-jet apparatus. A converging wall-jet apparatus for the study of fast response kinetics of ion-selective electrodes has been fabricated in this laboratory. The apparatus has no mechanically moving parts (except the solenoid valves), unlike the moving bar of the switched wall-jet apparatus of Linder et al.¹¹ Previous dynamic response measuring instrumentation has often suffered from two main limitations. The first limitation is that the methods

used to create an activity step have often fallen far short of the ideal instantaneous change in activity desired.^{1,2} The second limitation is the use of strip chart recorders^{38,39} or oscilloscopes^{40,41} as devices to measure the output signal. These devices have often not been fast enough to follow the very rapid voltage changes, have been too electronically noisy, have lacked the voltage measuring accuracy necessary for theoretical modeling of the electrode response, or, when fast enough, have not allowed an elapsed time sufficient to obtain the entire response curve to be measured.¹ We have developed an alternate design to the switched wall-jet apparatus, which we have called a converging wall-jet apparatus, which allows for the creation of very fast and reproducible activity steps and which incorporates fast digital data acquisition. This instrument incorporates a fast digital acquisition board with an analog to digital converter, a microcomputer, and software specifically written for the data acquisition and experimental control processes. This instrument is a transient signal analyzer capable of accurately measuring even the quickest dynamic responses of ISEs at an acceptable noise level. Furthermore, the basic design presented here can be easily modified to allow programming of multiple activity steps using more than two wall-jets. Such an improved design would allow for the creation of rapid and complicated activity steps in rapid succession of each other. The apparatus has been designed with the five following specifications in mind. First, it must allow activity steps of ions to be created in the range of tens of milliseconds. Second, it must allow for at least a 10 KHz data sampling rate to ensure for capture of all transients in the signal. Third, jet switching and data

acquisition must be precisely controlled in the time domain. Fourth, provisions must be made for data analysis (curve fitting) and data presentation (graphing of data, fitted curves, etc.). And fifth, upgrading should be possible with only minor modifications to the basic system. We seek to upgrade the system by building minor new subsystems, not a completely new instrument. A block diagram of the apparatus is shown in Figure 2-7. It can be seen that it is a computerized system using a "V" arrangement of the jets, such that the two streams converge at a common point at the surface of the membrane.

The solution delivery system. The solution delivery system is the heart of the apparatus and consists of several components. First, there are two 5 liter capacity reservoirs, constructed of 100 mm polyvinyl chloride tubing, which contain the test ion solutions under regulated nitrogen pressure. These are shown in Figure 2-8. Each reservoir has an end fitting at the bottom, a screw cap holder fitting at the top, and a screw cap to go into the holder. The end fitting and the screw cap fitting have been affixed to the 100 mm polyvinyl chloride tube by means of a primer for polyvinyl chloride pipes, and then using ordinary polyvinyl chloride cement. Contained within the screw cap are two machined fittings, made of Delrin. The first fitting allows connection by means of a Nalgene hose to the nitrogen tank so as to pressurize the reservoir. The second fitting connects to a polyethylene drainage tube which goes to the bottom of the reservoir and an external section of Nalgene hose which leads to a machined Delrin fitting screwed into the inlet of the solenoid valve. The solenoid valve outlet has a machined Delrin fitting which is the jet

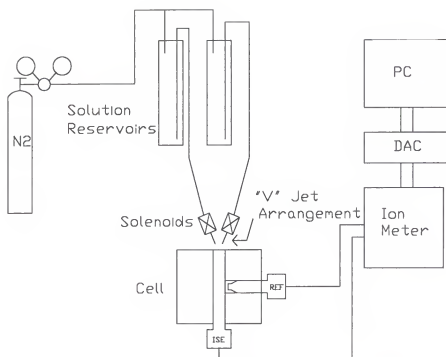


Figure 2-7. In situ non flow-cell (converging wall-jet) instrument for ISE dynamic response measurements.

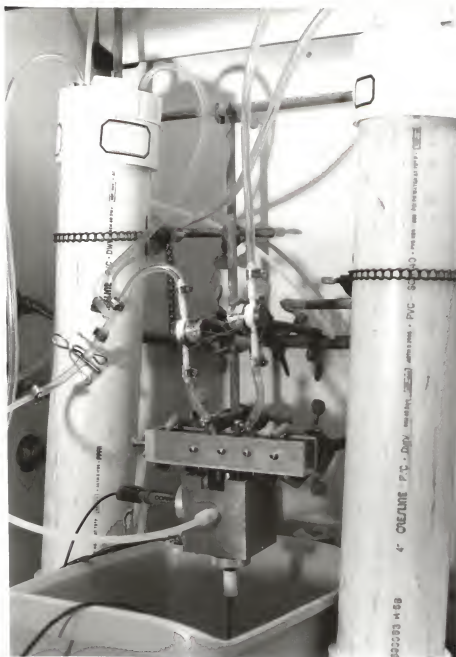


Figure 2-8. Photo of the converging wall-jet instrument. The solution delivery system and electrochemical cell are seen.

nozzle, which directs the flow of solution to the ISE membrane. The jets are arranged in a "V" geometry and allow the flow of solutions from the two reservoirs to converge at the top of the ISE electrode. The "V" geometry of the jets is shown in Figure 2-9. The flow of solution through the jets is switched by normally-closed solenoid controlled valves (Cole-Parmer Instrument Co., catalog number 01367-70). The voltage necessary to open the valves is supplied by a generic DC power supply, which has been designed and built by our electronics technical shop. This unit supplies power to a specially designed solenoid driver board built in-house by our electronics technical shop. The driver board is controlled by means of two digital output lines from the digital acquisition card, Advantech #PCL-812PG. The voltages on these lines are software triggered by a QuickBASIC program written by Dr. Vaneica Young, called KINETICS.BAS.

The electrochemical cell which holds the two electrodes. The electrochemical cell consists of a stainless steel electrode holder, the indicator electrode (ISE), and the reference electrode. The electrode holder has been made with the help of our machine shop technicians. The electrode holder can be seen in Figure 2-10. Cut through it are two bores in the body, one for each electrode, which meet at a 90 degree angle. In order to allow for electrical continuity between the indicator and reference electrodes, the bore to hold the indicator electrode has been machined 0.3 mm larger than the diameter of the indicator electrode. The electrodes are held in place by means of "O" rings, which are compressed by specially prepared threaded plugs screwed into the electrode holder. The



Figure 2-9. Photo of the converging wall-jet instrument. The "V" jet arrangement, the membrane of the ISE, and the waste drainage trench are seen.

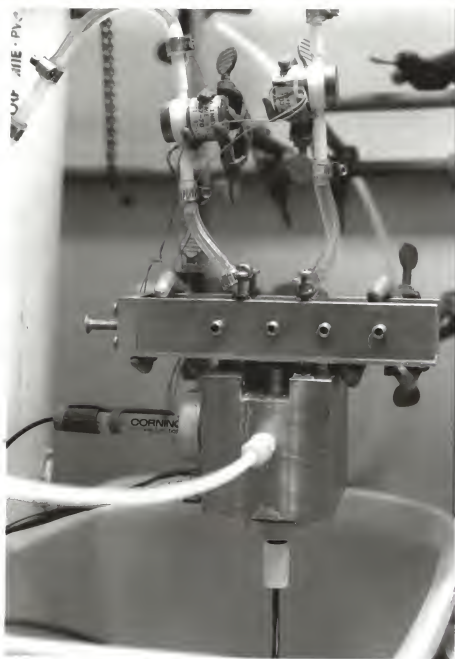


Figure 2-10. Photo of the converging wall-jet instrument. The electrochemical cell components (indicator ISE, reference electrode, and cell) are seen.

electrochemical cell that we have used follows closely that which Linder et al. described,¹¹ except that we have designed the drainage to waste differently. In our system, we have cut a circular trench around the steel holding the indicator membrane, and connected it to another trench which leads to the side of the block of steel. The overflow of the solution hitting the indicator membrane flows into the circular trench and over the side of the block. This can be seen in Figure 2-9.

The electronics used in the converging wall-jet apparatus. The potential of the indicator electrode relative to the reference electrode is measured using a Fisher Accumet model 750 ion analyzer. The analog signal from this meter is fed to a 12 bit successive approximation analog to digital converter (accuracy $0.015\% \pm 1$ bit) on the Advantech PCL-812PG card. There are three options for initiating an analog to digital conversion: software trigger, programmable pacer trigger or external pulse trigger. For these experiments we have used the programmable pacer trigger mode. Likewise, there are three analog to digital data transfer modes. They are program control, interrupt handler routine or direct memory access transfer. With direct memory access (DMA) transfer, a maximum sampling rate of 30 KHz is possible. At present, we are using program control, which limits the maximum sampling rate to 10 KHz, which we believe to be a sufficiently high sampling rate for most ISE applications. The digitized data are stored in a dynamically allocated array in the conventional RAM of the computer. The conventional RAM limitation of 640 kilobytes of memory imposed by MS-DOS limits the number of datum points which can be collected on any activity step to 10,000.

At our current maximum sampling rate of 10000 Hz, the minimum time resolution which can be obtained is 0.1 msec. After the last datum point is collected on any step, the data from the array are stored as a file on the personal computer's hard disk.

The purpose-designed experimental control and data processing program, KINETICS.BAS. The experimental control and data acquisition processes are accomplished by means of PCL-812PG driver subroutines, which have been incorporated in the RUN EXPERIMENT subroutine of KINETICS.BAS. This program also contains subroutines for saving the data to the hard disk, loading stored data from the hard disk, differentiating data, modelling data for the purpose of extracting rate constants and checking theoretical dynamic response models, and for graphing data. There is also a help menu, so that a novice can become familiar with the operation of the system.

The electrodes used to test overall system performance. In order to compare the performance of our apparatus with the performance of other wall-jet apparatuses, we have evaluated its performance by using iodide activity steps. A Corning iodide/cyanide electrode, catalog number 476127, has been used as the indicator ISE. We have used a Corning double-junction Ag/AgCl electrode, catalog number 476370, as the reference electrode.

Measurement of the time needed to begin creating activity steps. It is important to quantify the time needed for the system to create activity steps. There are four steps needed for the creation of a forward activity step. The first is the time

needed for the second solenoid valve to open and for the first solenoid valve to close. The second is the time needed for the second solution to begin reaching the ISE membrane. The third is for the second solution only to be reaching the membrane, and to wet completely the top of the outermost layer of the stagnant solution layer. The fourth is for the second solution to rinse away the remnants of the first solution completely. Of these individual quantities, the first is by itself unmeasurable. The author has devised a way to measure the time for the system to complete the first and second steps as well as the first, second, and third steps. The time needed to measure the removal of the first solution stagnant layer is also unmeasurable. For the measurable quantities, two conductivity "electrodes" have been designed. The first consists of an aluminum tube and a wire holder, machined from polyvinyl chloride, for two copper wires (diameter = 0.30 mm). This is shown in Figure 2-11. The two copper wires are aligned parallel to each other in the plane of the holder and are spaced about 1 mm apart so that a solution jet can make contact with both of them simultaneously at the center of the holder. The wires are connected to a voltage divider circuit such that when an electrically conductive solution contacts both of the wires, a voltage change will occur and be measured by the digital acquisition board. The circuit is shown in Figure 2-12. The source voltage is 12 volts DC. This is passed through a voltage divider consisting of two resistors, whose values have been chosen to divide the source voltage into 11 volts across the top of the voltage divider and 1 volt across the bottom of the voltage divider. The conductivity cell is wired in parallel to the voltage divider across the 1

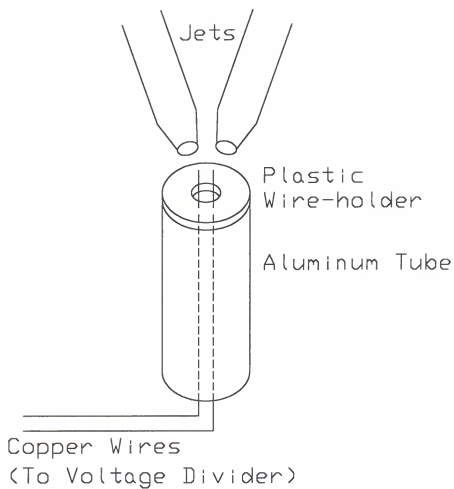


Figure 2-11. Conductivity cell used to measure the time needed to begin creation of activity steps.

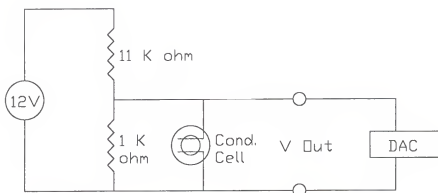


Figure 2-12. Electronic schematic diagram of circuit used with conductivity electrodes to measure the timing of activity step creation.

volt (bottom resistor) segment. The voltage across the conductivity cell is measured by the digital acquisition board, digitized at 10000 Hz, and stored to the computer hard disk. A sodium chloride solution has been used as the conductive solution. At first, the voltage measured by the digital acquisition board is nominally 1000 millivolts. When the salt solution reaches the two copper wires of the conductivity cell, the resistance of the conductivity cell is added in parallel to the voltage divider circuit. The result is that the voltage measured by the digital acquisition board suddenly and sharply drops. By looking at where this voltage drop occurs, one can determine when the first instance of the salt solution has hit the two wires. Using this method, we have devised an experiment that allows us to use this cell to measure the time it takes the system to initialize an activity step. For this measurement, one reservoir is filled with deionized water and the other reservoir is filled with a 10 gram per liter sodium chloride solution. With the deionized water jet hitting the wires, the path between the wires is not conducting. A signal from another QuickBASIC program written by Dr. Vaneica Young, TESTA.BAS, switches the flow of sodium chloride solution on. When the salt solution from the second reservoir hits the wires they become conducting. This causes the aforementioned voltage change in the voltage divider circuit which is measured by the digital acquisition board. The time that has elapsed will account for the time needed to switch the salt water line's solenoid on, for the stream to travel from the jet nozzle to the wire holder, make contact with the wires and complete that circuit. This simulates the time needed for the second solution of a real activity step to begin

striking the ISE membrane, and thus is a measure of the time needed to begin creating a real activity step with a real ISE. We have used replicate measurements to provide for a measure of both the average time needed to begin creating an activity step as well as give some measure of the reproducibility of the same. The results are given in the results and discussion section.

Measurement of the time needed to cover the outermost stagnant layer with the second solution. In the second conductivity electrode, two copper wires are aligned parallel to the aluminum tube and are spaced 8 mm apart, this distance simulating the diameter of common ISE membranes. This holder is used to measure the time needed for a second solution to displace the outermost stagnant layers of the first solution, thus continuing but not completing the activity step. One reservoir is filled with deionized water and the other reservoir is filled with a 100 gram per liter sodium chloride solution. The more concentrated salt solution in this case is necessary due to the minimal amount of exposed copper, and the rather thin film of salt solution that must complete the circuit between them. No voltage change will be observed in the voltage divider circuit until the sodium chloride solution has completely covered the outermost stagnant layers of the 8 mm diameter circle, simulating coverage of an 8 mm diameter ISE membrane. The second type of conductivity cell is shown in Figure 2-13. The conductivity electrode is placed in the bore which normally holds the indicator electrode, and the reference electrode is not used.

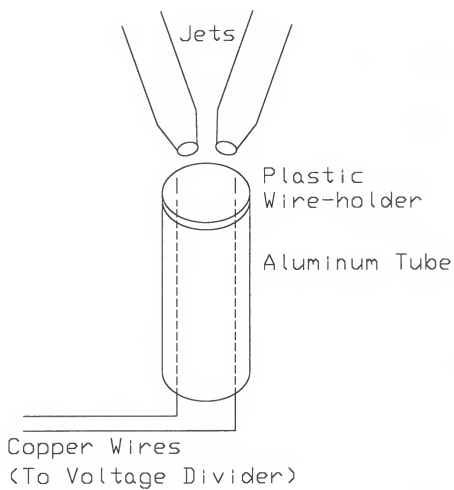


Figure 2-13. Conductivity cell used to measure the time needed to replace the topmost part of the stagnant layer with the second solution.

Fabrication of the apparatus. This section describes the unique parts of the converging wall-jet apparatus that were built in our technical shops, what materials were used to build them, and how they were built. The solution reservoirs were fabricated from 100 mm polyvinyl chloride pipe and fittings obtained from a hardware store. The end cap and screw cap were primed with a polyvinyl chloride pipe primer obtained from a hardware store. They were then cemented together with polyvinyl chloride pipe cement obtained from a hardware store. The assembled reservoir was then allowed to dry for 48 hours. The screw caps needed two holes to be drilled through them to allow for two fittings machined of Delrin to be fastened through the screw caps. The two fittings themselves were turned on a lathe, bored with a drill bit and then a reamer, and finally external screw threads were cut using a die on a portion of the fittings. They are sealed by the use of "O" rings, and a nut serves to tighten the fitting onto the screw cap. One fitting per screw cap is connected by a hose clamp to a Nalgene hose and to the regulated nitrogen tank. The other fitting in the screw cap is connected by a nalgene hose to a tube that is screwed into the solenoid valve. This tube was made of Delrin, cut on a lathe, bored using a drill bit and then a reamer, and external screw threads were then cut with a die. It screws into the inlet of the solenoid valves. The outlet of the solenoid valves has the jets screwed into them. They were made from Delrin, cut on a lathe, bored with drill bits and a reamer, and then a section of external screw threads was cut using a die. The external section of the ends opposite the threaded portion were cut on a lathe to a slight taper. An aluminum block was made to hold the

two jets and is held in place at the top of the cell by means of a holder. The block was cut of aluminum on a mill, and two holes were drilled and reamed for the jets to fit through. The holder for the block is connected by four machine screws to the top of the electrochemical cell. This constituted the solution delivery system. The electrochemical cell was also machined in our technical shops. The cell was cut from a cube of stainless steel. The cube was made by cutting a section of rod stock on a band saw, cutting this on a lathe until the length was correct, and then forming a rough cube shape by trimming away the excess by using a band saw. This rough cube was then cut using a mill to a cube of the correct dimensions. The two bores for the electrodes were then cut. This was done on a lathe using drill bits to get the approximate bore. The bore for the indicator ISE was cut with a reaming (interior) bit on the lathe to the exact dimension needed. The bore for the reference electrode did not need such precision and was cut with a reamer. Interior screw threads were cut at the end of each bore with a tap. A plug was fitted into each of these threaded bores to hold an electrode in place. These plugs were made of aluminum. They were turned on a lathe, bored with a drill bit and then a reamer, and then knurled on the knob end. The narrower end was cut for external threads using the lathe. The threaded end was cut at a 45 degree angle on the interior of the bore so that when the screw plug contacts an "O" ring, it will compress onto the body of the electrode passing through the bore of the screw plug.

Results and Discussion

The results of the experiments used to measure the time needed to initiate an activity step with the converging wall-jet instrument. The method used for this measurement has been described in an earlier paragraph of this chapter. The conductivity cell shown in Figure 2-11 and the voltage divider circuit shown in Figure 2-12 were used. A 10 grams per liter sodium chloride solution has been placed in reservoir one. The solution in reservoir two is deionized water. The variable in the experiment is the pressure of nitrogen used to fill the reservoirs. As the pressure increases, so does the linear rate of flow of the solutions, and the distance from the jet nozzle to the conductivity cell wires is spanned in less time. We have used test pressures of 10, 20, 30, 40, 60, and 80 pounds per square inch (PSI) of nitrogen. The software to control the switching of the solenoids and data collection was written by Dr. Vaneica Young using QuickBASIC and is called TESTA.BAS. This program was specifically written for the characterization of the timing of the activity step creation for the converging wall-jet apparatus. The other program, KINETICS.BAS, is used to collect real ISE data. The data that we have collected are shown in Table 2-1. The time measured (delay time) is the time interval between the instant the TESTA.BAS program gives the signal to switch the solenoids until the salt solution has reached the conductivity cell. Figure 2-14 shows some data taken at 80 PSI. The voltage is sampled at 10000 Hz and is plotted versus time. Eight measurements were taken at each pressure setting, thus

Table 2-1. Timing data collected for converging wall-jet instrument.

File Group	Nitrogen Pressure, PSI	Average Delay Time, msec ^a	Standard Deviation	Range Of Data
A2701	10	10.76	0.81	0.6
A2721	20	8.99	0.24	0.7
A2741	30	8.99	0.19	0.6
A2761	40	8.41	0.24	0.6
A2781	60	6.78	0.24	0.7
A2901	80	6.54	0.24	0.8
File Group	Nitrogen Pressure, PSI ^b	Average Coverage Time, msec ^c	Standard Deviation	Range Of Data
A3001	10	12.04	0.41	1.3
A3021	20	10.13	0.19	0.6
A3041	30	9.46	0.24	0.8
A3061	40	8.71	0.20	0.7
A3081	60	7.39	0.27	0.8

a) Delay time measured using first conductivity cell.

b) The data set for 80 PSI using the second conductivity cell was not collected.

c) Coverage time measured using second type conductivity cell.

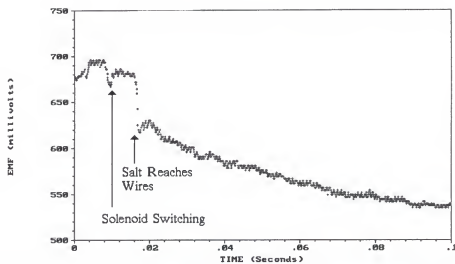


Figure 2-14. Plot of voltage versus time for measurement of time needed to begin an activity step.

we can speak of the statistical results of the data also. It can be seen that the standard deviation and range for each set of eight datum points at a given pressure are relatively low. This shows that the converging wall-jet apparatus produces very reproducible datum points within a trial. The exception to the latter statement is all data at 10 PSI show a larger standard deviation and range. Clearly, the effects of a low linear rate of flow due to the low pressure of nitrogen have decreased the precision of the time needed to initiate creation of activity steps. The average time delay decreases as the pressure increases, as is expected. A graph of the data is shown in Figure 2-15. It can be seen from the shape of the curve that at the higher pressures used, a leveling of the time delay can be seen. If still higher pressures were to be used with the converging wall-jet instrument, the delay time would still be approximately the same as at 80 PSI. The reason for this is probably due to the first step of the four needed to create an activity step with the converging wall-jet apparatus, namely the time needed to switch the solenoids. The solenoid valves are likely to require a constant amount of time to open up until a reasonable flow of solution begins. This is because the solenoid valves receive a unchanging voltage and current signal to operate the electromechanical valves. The graph shown in Figure 2-15 seems to justify the possibility of a constant time needed to operate the solenoid valves, this time being approximately 5 milliseconds. The behavior seen could be due to other possibilities such as nitrogen leaks in the reservoirs. The reservoirs leak more air than had been anticipated. The leaks could cause a relatively large day to day variance for the delay times at the same base pressure.

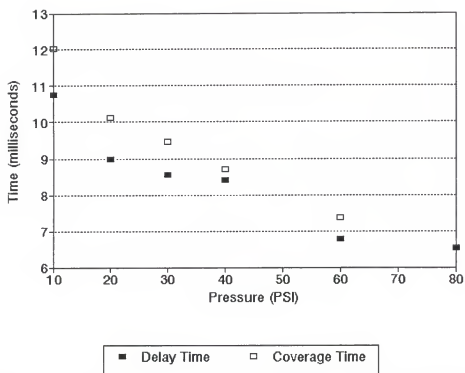


Figure 2-15. Plot of time versus pressure for converging wall-jet apparatus timing experiments.

The author has not yet collected enough time delay data to make any statement about the real day to day variance of the time delay of the system. If the experiment were repeated with a better sealed reservoir made of metal, then the leveling of the time delay data at high pressures can be confirmed and is very likely due to a constant switching time. Also, it is likely that the standard deviation and range of the delay time at a given pressure would decrease. The minimum time needed to initialize an activity step for our system was recorded at 80 PSI and was 6.0 milliseconds. These are the data shown in Figure 2-14. This level of performance is comparable to other claims of instrument performance. Linder et al. measured 7 milliseconds as the time needed to move the jets in their switched wall-jet instrument.¹¹ We have characterized the time delay behavior of our system through many samplings and have shown that our instrument is highly reproducible in the delay time at all but the lowest operating pressures. Additional advantages of the converging wall-jet apparatus include a higher sampling rate for data and simpler construction than the switched wall-jet apparatus. In the future, programmed, multi-step changes of activity of more than two different solutions will be possible with the converging wall-jet instrument.

The results of the experiments used to measure the time needed to cover the outermost stagnant layer with the second solution using the converging wall-jet instrument. The method used here has been described earlier in this chapter. The conductivity cell shown in Figure 2-13 and the voltage divider shown in Figure 2-12 are used in this experiment. All other experimental conditions replicate those stated

in the previous paragraph. The results are shown in Table 2-1, and also plotted in Figure 2-15. The set of data at 80 PSI was not collected. The effect of increasing pressure is to decrease the time needed to cover the outermost stagnant layer with the second solution (coverage time). Once again, the standard deviation and range for each pressure trial are small except for the 10 PSI data. Looking at Figure 2-15, one can see that the coverage time is only a small addition to the delay time. There is only a very slight difference in the time needed to initialize the activity step and to provide coverage of the outermost stagnant layer. It is unfortunate that one cannot measure the time needed to remove the last remnants of the first solution by the second by experimental technique. The time to truly create an activity step at the surface of the ISE membrane will be the coverage time plus the time needed for the additional processes of diffusion and convection to completely displace the first solution with the second. These events could take many milliseconds of additional time, and could depend on such factors as electrode surface roughness, solution viscosity, and the thickness of the stagnant layer. If these last events can be measured, then the real time to create an activity step could be stated for the converging wall-jet instrument.

Performance of the converging wall-jet apparatus to steps in iodide activity using an iodide electrode. We have tested the time performance of the converging wall-jet apparatus using a Corning iodide/cyanide ISE (catalog number 476127) in combination with a Corning double junction reference electrode (catalog number 476370). The experimental conditions used were as follows: nitrogen pressure, 40

PSI; data sampling rate, 10 KHz; datum points collected, 10000. The first solution was 1.00×10^{-3} molar sodium iodide. The total ionic strength was adjusted with potassium nitrate to 0.15 molar. The second solution was identical except the sodium iodide was 1.00×10^{-2} molar. Analytical grade reagents from Fisher were used to make the solutions. De-ionized water was used as the solvent. The resulting potential versus time behavior (file IKIN 3607) is seen in Figure 2-16. The response is quite rapid, and the voltage has stabilized within 250 milliseconds. An interesting artifact is seen in the dynamic response. The voltage changes very rapidly initially. A second region characterized by a somewhat slower response is also seen. Furthermore, the total voltage change is 70 mV, somewhat higher than the expected change of 59 mV. The reasons for the two rates at which the electrode responds and the slightly higher than expected voltage are not clear at this point, but may be caused by the "breaking in" of the new iodide ISE used in this experiment. There are few ions that interfere with the iodide electrode in the static mode of operation, and we do not suspect contamination by these ions as the cause of the unusual behavior. The change in voltage for the first region is roughly Nernstian, being about 51 mV. The time needed to reach a full scale voltage change is comparable to the data shown by Pungor and co-workers for another iodide ISE.¹¹ They showed the response to a full scale decade forward step occurring in about 100 milliseconds.

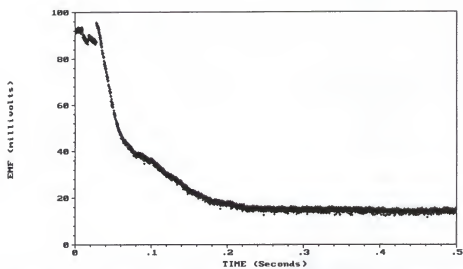


Figure 2-16. Dynamic response of the iodide ISE to a forward step in iodide ion.

CHAPTER 3

THE DYNAMIC RESPONSE OF THE FLUORIDE ION-SELECTIVE ELECTRODE

This chapter will show the results of experiments using the activity step method in combination with the converging wall-jet instrument to measure the dynamic response of the fluoride ion-selective electrode. Previous to our work, few true dynamic response measurements of the fluoride ISE have been recorded, and the only studies of the effects of interferent species on the fluoride ISE dynamic response have been performed with instrumentation inferior to the performance of the converging wall-jet instrument. The converging wall-jet instrument has been used to measure the true dynamic response of the fluoride ISE to tenfold steps in fluoride ion at constant total ionic strength. Also, the dynamic response of the fluoride ISE to certain other ions--chloride, bromide, hydroxide and cyanide--has been measured. These ions were chosen because their protonated forms appear in the dispersion plumes of halon extinguished armored fighting vehicle fires. Of these, only hydroxide has been reported as a static case interferent ion. In fact, very few studies of interferent effects on the dynamic response for any ISEs have appeared in the literature. Although chloride, bromide and cyanide are not static case interferents for the fluoride ISE, they could have a transient effect on the potential response. Transient effects, which alter the shape of response curves,

must be considered in the development of a real-time hydrogen halide gas analyzer. In each case, dynamic response measurements have been made for both forward and reverse activity steps.

Previous Studies of the Fluoride Ion-selective Electrode

The lanthanum fluoride based fluoride ISE. Ion-selective electrodes used to measure free fluoride activities in solution are all based on a solid-state membrane of LaF_3 . The electrode can be made so that all of its components are solid-state. Such an electrode would be used together with an additional, external reference electrode. Orion also makes a combination fluoride ISE, which is used without an external reference electrode. A third configuration, the ionic contact fluoride ISE, is no longer commercially available. Solid-state fluoride ISEs can be used from mildly acidic to mildly basic conditions, in the range of pH four to nine.⁴² Their concentration range spans several decades, typically in the range of 1×10^{-1} to 5×10^{-6} molar activity of fluoride ion.⁴² Their voltage as a function of activity of free fluoride ion is described by the well known Nernst equation. In the presence of interferent species, the voltage is given by the Nicolsky equation^{27,30}

$$E(a_i, a_j) = E_i^0 + S \log(a_i + \sum_j K_{ij} a_j^{Z_i/Z_j}) \quad (3-1)$$

where i indexes the primary ion and j indexes the interfering ion(s). Here the activities are given by a , K_{ij} is the selectivity coefficient for the j th (interferent) ion

to the i th (primary) ion, and Z refers to the ionic charges. The value of S is given by the gas constant R multiplied by the temperature in Kelvin divided by the Faraday constant and divided by the number of moles of electrons transferred in the reaction. For the special case of halide ions, the Nicolsky equation reduces to

$$E(a_i, a_j) = \text{constant} + S \log (a_i + \sum_j K_{ij} a_j) \quad (3-2)$$

because all ionic charges are unity. The lanthanum fluoride based fluoride ISE is a robust electrode. The static selectivity coefficient K_{ij} of the hydroxide ion, the only reported interferent ion, is 0.10.⁴² The term apparent selectivity is another measure of selectivity, and is equal to the reciprocal of the selectivity coefficient. The apparent selectivity of fluoride ions over hydroxide for the fluoride ISE is therefore 10. Al^{+3} and Fe^{+3} can form complex ions with fluoride and so can mask the presence of fluoride ion.⁴³ To prevent this, ionic strength adjustment buffers (ISAB) often contain compounds that will complex the aluminum and iron ions but not the fluoride ions.⁴³ The ionic strength adjustment buffer also serves the extremely important function of keeping the total ionic strength of the solutions analyzed very nearly constant. This is necessary as the activity of the fluoride is determined, not the concentration, and the activity varies as a function of the total ionic strength in the solution. The stability of the lanthanum fluoride based fluoride ISE is excellent, and is in the range of a few millivolts per day when used in the static mode of operation.⁴² The time needed for the electrode to reach the equilibrium voltage in

the dipping mode of operation is typically less than 1 minute. The dynamic response has been measured to be as rapid as 110 milliseconds.⁶ However, the response time can increase significantly due to the surface condition of the membrane.^{6,31,43,44} An accepted method of restoring the surface of the membrane includes polishing.^{31,44} The lanthanum fluoride based fluoride ISE is commonly used to analyze for fluoride content in tap water,⁴⁴ industrial waste water,⁴² brines,⁴⁵ and other aqueous solutions.⁴² The fluoride content in foods and beverages⁴⁴ such as wine⁴⁶ is often determined with the use of fluoride ISEs. They have also been used to measure fluoride content in soil extracts,⁴² biological tissue digests,⁴² serum⁴² and urine.⁴⁴ Use of the fluoride ISE in potentiometry is considered to be one of the easiest and least expensive methods used to determine fluoride ion content. When used as a detector in the flow injection analysis technique (FIA),^{43,44,47,48} the analysis of fluoride content with a fluoride ISE can be considered to be rapid as well, if the fluoride ISE detector itself is sufficiently rapid. However, spectrophotometric and amperometric detectors are often faster. The selectivity for fluoride is good in the dipping mode of analysis, and the sensitivity is adequate for many applications. In fact, simultaneous determination of fluoride, chloride, bromide, and iodide has been demonstrated with a multi-electrode FIA system.⁴⁹ Since many more samples can potentially be analyzed per hour with automated techniques such as FIA than by the static mode of operation done by hand, the response time of the electrode after rapid changes in fluoride activity is of interest both from a theoretical and practical viewpoint. Measurements of the dynamic response of the fluoride ISE can be used

to help determine the practical upper limit of samples analyzed per hour using FIA. The lanthanum fluoride membrane ISE has been used with FIA to determine up to 360 samples per hour, a rate equaling one sample every 10 seconds.⁵⁰

Dynamic response measurement of the fluoride ISE by Mertens et al. The only earlier study of the true dynamic response behavior of the fluoride ISE was conducted by Mertens et al.⁶ The authors looked at the transient voltage behavior of three different fluoride ISEs after submitting them to steps in fluoride ion activity. The authors built a Perspex "conical vacuum chamber" instrument of the in situ nonflow-cell type capable of creating rapid activity steps. The traces were recorded with a memory oscilloscope for short duration transients and a strip chart recorder for longer duration responses. Several different solutions containing fluoride ion were used ranging from 1.0×10^{-5} to 1.0×10^{-2} molar fluoride. The solutions were prepared from reagent grade NaF and an ionic strength adjustment buffer. Both forward and reverse activity steps were recorded. Six forward and six reverse steps were measured in all. Two commercial electrodes and one home-made electrode were studied. None of the electrodes was completely solid-state, and one of the commercially available electrodes was severely scratched on the surface. They saw that for a single pair of solutions the response was faster in the forward direction. For tenfold steps of activity of fluoride, the ratio of reverse response time to forward response time was in the range of 0.9 to 6.3, nominally two. Other research efforts corroborate these findings, and have indicated an average of about two for this ratio.^{1,2,36,51,52} The range of the ratios was greater using t_{50} values than

t_{90} values. For steps of two or three decades, the ratio of the reverse response time to the forward response time was much greater than two, and reached values as high as 75. The largest values of this ratio were reported for a three decade step, with the values for two decade steps being of intermediate values. Once again, the ratios calculated using t_{90} are probably closer to the true values than are the ratios calculated using t_{50} . The range of the ratios is greater for the t_{50} ratios. Surprisingly, when comparing ratios of reverse response time to forward response time, all three of the electrodes gave similar ratios, the more important factor being the magnitude of the activity step. The fastest electrode in general was the commercial electrode with a smooth surface. Its response times were typically five to 20 times faster than the other two electrodes. The scratched electrode and the home-made electrode were about equal in their time response characteristics. The fastest t_{50} that they saw was 12 milliseconds, for a step of 1.0×10^{-5} to 1.0×10^{-2} molar fluoride with the smooth membrane commercial electrode. The t_{90} for the same step was 110 milliseconds. The slowest response was for the reverse step of the same two solutions, but with the home-made electrode. The t_{50} and t_{90} were 6.0 and 79 seconds respectively. In the forward direction, activity steps ending at higher activities of fluoride responded faster than those ending at lower activities, regardless of the initial activities of fluoride. No definite conclusion could be drawn from the results of the reverse activity steps. For those steps in which t_{90} was less than 2 seconds a hyperbolic (not exponential) function fit the data the best. The ratio of t_{90} to t_{50} for all the activity steps given by the authors ranged from 6.7 to 300,

a considerable spread. The authors also noted that the electrode response was fastest when the flow rates of the solutions were highest. The authors attributed this effect to slow diffusion of fluoride ions from the bulk solution through the hydrodynamic layer to the membrane surface. The important point of this research is that when using an instrument capable of creating very fast activity steps, a response time of the electrode was measured in the range of 100 milliseconds, and a response time of that order of magnitude is representative of a true dynamic response time, not a static response time. The following papers did not use instruments as capable of creating fast activity steps as Mertens et al., and all of these authors have cited response times (if reported) for the fluoride electrode in the range of a second or more.

A study of several ions that complex fluoride ion by Frenzel and Bratter.

Frenzel and Bratter looked at the effects of several complexing ions of fluoride with the fluoride ISE.⁴³ The ions studied were Al^{+3} , Mg^{+2} , Fe^{+3} , Ca^{+2} , and Si^{+4} . The authors also studied the effect of pH on the transient response of the fluoride ISE. The authors used a modified FIA instrument for their study, and while their instrument is not as capable of measuring true dynamic response as a wall-jet instrument is, their study is nevertheless a very interesting one. Because the modified FIA instrument is an ex situ flow-cell instrument, their measured time responses are probably intermediate between dynamic and static response times. The authors first measured the response times for steps in fluoride ion only. Their shortest t_{50} and t_{90} were 980 milliseconds and 3760 milliseconds respectively for a

three and a half decade forward step change in fluoride activity. The longest response times were over 5 minutes for some of the reverse steps. By comparison, the responses that Mertens et al. report are significantly faster than those reported by Frenzel and Bratter, typically an order of magnitude faster. While small differences in behavior might occur for electrodes purchased from different manufacturers or might be due to differences in the surface conditions of the membranes, et cetera, these variables cannot explain the order of magnitude differences discussed above. Instead, the difference between the two sets of results can be explained by the slower creation of activity steps and the greater hydrodynamic layer thicknesses which occur with the FIA setup. Indeed, Frenzel and Bratter showed that the response time is an increasing function of solution viscosity. The authors looked at the effect of changing the ionic strength of the carrier solution on the voltage signals obtained. They saw non-monotonic behavior in some of these experiments, and increasing response times in others. However, even at constant fluoride activity and constant total ionic strength, a change in the salt used to make the ionic strength adjustment buffer affected the signal obtained. The authors offered no explanation for the non-monotonic transient behavior. They also reported non-monotonic behavior during very basic conditions and also during very acidic conditions. The authors noted that calcium, magnesium, aluminum, and silicon can form complex ions with fluoride and may cause non-monotonic behavior.

The Results of Other Authors Who Have Experimented With Fluoride ISEs as Detectors in FIA Systems or Static Mode Experiments

Najib and Othman. Najib and Othman have performed simultaneous analysis of fluoride, chloride, bromide, and iodide using a modified FIA instrument, four ISEs, and selective removal of unwanted species via chemical reactions with columns.⁴⁹ In their study, interferents have been dealt with by chemical reactions and with some chemometric methods employed. This was not a study of the dynamic response of interferent species with regard to ISEs, but this study did, however, deal with the problem caused by mutual interference amongst the halide ISEs. The authors were able to analyze successfully all four of the aforementioned halides with a good degree of accuracy. They employed suppressor columns to remove interferents selectively upstream of the ISEs in combination with split streams of carrier solution and analyte. Even though capable of only very crude dynamic response measurements for the halide ISEs, the authors reported t_{95} values in the range of nine to 30 seconds, and this seems to be typical of FIA response times. The authors noted that if the electrode response became sluggish, the passage of 1×10^{-3} M analyte solution for several hours through the instrument could recondition at least some of the ISEs. In more severe cases of contamination caused by interferent species, polishing of the electrode surface was necessary to recondition the surface of the ISE. Since in FIA the analyte passes over the ISE membrane for only a very brief period of time, the effect of interferences could possibly be reduced if the rate of electrode response to the primary ion is much

greater than to the interferent ion. Of course, the effects of interferents would be greater if the rate of electrode response to the interferent is much greater than to the primary ion. This is one of the reasons why our efforts have been directed at measuring the dynamic response of both primary and suspected dynamic case interferent species. Najib and Othman have shown that the selectivity coefficients of the primary/interfering ion pair are often quite different in FIA than what has been determined by static ISE experiments. In some cases FIA selectivity coefficients are smaller, and in other cases they are larger than the corresponding static case selectivity coefficients.

Cammann. Cammann used a seven ISE cell in combination with FIA to analyze drinking water samples.⁵³ The use of a fluoride ISE to indirectly determine the presence of Al^{+3} was described. Cammann noted the aforementioned kinetic discrimination effect that can drastically change the selectivity coefficient of the primary/interferent ion pair, and also noted that chemical reconditioning of the ISE membrane is possible by the flow of primary ion over the membrane. Cammann noted that the direct potentiometry of halide ions generated by bombardment of organohalogen compounds with UV radiation is possible.

Frenzel and Bratter. In another publication, Frenzel and Bratter used FIA for the determination of fluoride in tap water, wine, tea, and other beverages.⁴⁴ The authors were able to analyze up to 40 samples per hour. This sampling rate implies a response time of no greater than 90 seconds for the fluoride ISE. They indicated that the surface condition of the electrode membrane could change the slope of a

calibration plot, and that polishing would return the electrode to its initial value of slope. To overcome the effect of large amounts of complexing ions such as Al^{+3} , the ionic strength adjustment buffer was optimized for certain conditions.

Van Oort and Van Eerd. Van Oort and Van Eerd studied the effect of surface roughness on fluoride ISE dynamic response.³¹ The activity step method was used with an instrument of the ex situ flow-cell type. The activity steps thus created were less than ideal. The authors did measure the t_{63} of unpolished and freshly polished membranes for both forward and reverse activity steps. Fluoride concentrations ranged from 10^{-1} to 10^{-6} molar. Polishing was accomplished using very fine alumina powder. They typically found values of t_{63} of 10 seconds for forward steps and about 20 seconds for reverse steps. Polishing the surfaces was shown to decrease the response times, but only in methanol/water solutions. Polishing was shown to have minimal effect on the response times in pure aqueous solutions. The shortest response time measured was 6 seconds for the step from 10^{-3} to 10^{-2} molar fluoride.

Ilcheva et al. Ilcheva et al. studied the effect of addition of fluoride in the carrier solution in FIA to reduce the response time for more rapid analysis.⁵⁰ Their instrument was a hybrid of the ex situ flow-cell and ex situ nonflow-cell types. They found that the addition of fluoride into the carrier stream decreased the response time of the electrode, with no added fluoride leading to the longest response times. They were able to achieve a maximum sampling rate of 360 samples per hour. This sampling rate would correspond to a response time of 10 seconds or less.

Frenzel. Frenzel described the use of FIA and ion selective electrodes, including the fluoride ISE.⁵⁴ In this paper the fluoride ISE voltage was shown to drift about 8 millivolts per minute. In static ISE usage, the amount of voltage drift is minimal. Frenzel demonstrated that in cases where the fluoride solution is rapidly flowed over the fluoride ISE, drifting voltage response may occur. Frenzel did not state what the cause of the drifting response might be.

Thompson and Rechnitz. Thompson and Rechnitz used a fluoride ISE as part of an instrument used to measure the kinetics of fast chemical reactions involving the fluoride ion.³³ Both the continuous flow and stopped-flow techniques were used. Their instrument was of the ex situ flow-cell type. The response time of the electrode itself was not measured, but rate constants in excess of $10000 \text{ M}^{-1} \text{ sec}^{-1}$ were predicted to be measured with their system.

Buffle and Parthasarathy. Buffle and Parthasarathy modeled the response of the fluoride ISE using data collected from the immersion and injection techniques.³ They stated that when the electrode response time is in the range of milliseconds, the rate determining process is diffusion. The authors postulated that formation of a hydroxide layer may alter the response kinetics of the fluoride ISE. However, they rejected this hypothesis because they claimed that electrode kinetics are unchanged after pre-treatment in an acidic solution. Unfortunately, they presented no experimental evidence in support of this claim.

Jackson et al. Jackson et al. used ISEs to determine indirectly the hydrogen halide and hydrogen pseudohalide content of air samples taken from manufacturing

sites.⁵⁵ Analysis of HF, HCl, HBr, and HCN were performed on 30 liter air samples made into a solution volume of 25 ml. The analyses were performed sequentially with the dipping mode of ISE operation. Accurate readings of the halide content could be measured at the microgram per milliliter level (ppm).

Duff and Stuart. Duff and Stuart determined the halide content of orthophosphate minerals using sequential dipping mode measurements using ISEs.⁵⁶ Fluoride, chloride, bromide, and iodide were determined. The effect of mutual interference of the chloride, bromide, and iodide ISEs was discussed at length. The authors noted no interference of the fluoride ISE from the chloride, bromide, or iodide content.

Trojanowicz and Lewandowski. Trojanowicz and Lewandowski developed a flow-through system for the simultaneous determination of fluoride, chloride, nitrate, and ammonium ion content in tap and river water.⁵⁷ Though not a FIA instrument, it shared some of the characteristics of one. The analysis of fluoride and chloride was performed on the same stream of analyte. The analyte had been mixed with an acetate buffer containing hydrogen peroxide. The authors did not mention any interferences regarding the fluoride or chloride analyses with this arrangement.

Experimental

Apparatus

The converging wall-jet apparatus described in Chapter 2 has been used for all fluoride ISE data collection reported here. For experiments involving the

fluoride ISE, we have used sampling rates of 100 and 10000 Hz. The slower sampling rate was used for experiments in which the voltage data were collected for more than 1 second, to prevent a data file composed of greater than 200 kilobytes of data. This was to prevent data files which would exceed the available RAM memory in the MS-DOS microcomputer used for data collection. The duration of sampling was always one, 10, or 20 seconds. The 1 second duration experiments were always at a sampling rate of 10000 Hz, while the 10 and 20 second duration experiments used a sampling rate of 100 Hz. The pressure of the nitrogen used to charge the solution reservoirs was 30 PSI, which resulted in a moderate solution flow rate through the jet nozzles. We had tested the time to initiate the creation of activity steps (shown earlier in Chapter 2) and found the result to be about 9 milliseconds at 30 PSI of nitrogen. We felt that using a higher nitrogen pressure would result primarily in faster use of the fluoride test solutions, with the slight decrease in time to initiate an activity step at higher pressures being of lesser importance.

Electrodes

Two electrodes were used for all of the fluoride ISE experiments. We have used a Corning double-junction Ag/AgCl electrode, catalog number 476370, as the reference electrode. A new Corning fluoride ion selective electrode, catalogue number 476042, of the LaF_3 membrane type has been used as the indicator

electrode. Both electrodes were used in their unmodified state, except for 1 hour of preconditioning of the fluoride ISE with our fluoride solution one.

Solutions

A total of five different fluoride containing solutions have been made for our experiments with the fluoride ISE. All of these solutions have a total ionic strength of 0.100 molar activity, using added reagent grade KNO_3 to adjust the ionic strength when necessary. All species are given in terms of molar activity, having the effect of ionic strength taken into account. All solutions were made using deionized water as the solvent. The compositions of these solutions are given in Table 3-1. Solution one was 1.0×10^{-3} molar in fluoride, using reagent grade KF, and had its total ionic strength adjusted to 0.100 M using reagent grade KNO_3 . Its pH is eight, slightly basic, caused by the weakly basic KF. Solution two used the same reagents, but had a fluoride activity of 1.0×10^{-2} M. Solution three had large concentrations of both fluoride and hydroxide ions. It was 1.0×10^{-3} molar in fluoride, using KF as the reagent, and 7.4×10^{-2} molar in hydroxide, using KOH as the reagent, with the ionic strength adjusted to 0.100 molar using KNO_3 . The pH of this solution is 12.87. We have weighed the KOH directly, taking into account the inert materials and impurities present in the reagent. This was sufficient for a two digit accuracy for the activity of hydroxide in the solution. Solution four had fluoride, chloride, and bromide ions present. It was 1.0×10^{-3} molar in fluoride, using reagent grade KF as the source of fluoride. It was also 4.5×10^{-3} molar in both chloride and

Table 3-1. Compositions of solutions used with the fluoride ISE.

Solution	a_{F^-} , M	a_{OH^-} , M	a_{Cl^-} , M	a_{Br^-} , M	a_{CN^-} , M
1	1.0E-3	1.0E-6	0	0	0
2	1.0E-2	1.0E-6	0	0	0
3	1.0E-3	7.4E-2	0	0	0
4	1.0E-3	1.0E-6	4.5E-3	4.5E-3	0
5	1.0E-3	2.5E-2	3.0E-3	3.0E-3	3.0E-3

bromide, using reagent grade NaCl and NaBr as reagents. The ionic strength was adjusted to 0.100 using reagent grade KNO_3 . The pH is eight, slightly basic, due to the presence of KF. Lastly, solution five contains fluoride, chloride, bromide, hydroxide, and cyanide. The activity of fluoride is 1.0×10^{-3} molar using reagent grade KF. The chloride and bromide activities are each 3.0×10^{-3} molar using reagent grade NaCl and NaBr respectively. Hydroxide is present at a molar activity of 2.5×10^{-2} , using reagent grade KOH as the source. Cyanide is present with a molar activity of 3.0×10^{-3} , using reagent grade KCN as the source. This reagent must be added after the KOH, to prevent significant formation of toxic HCN. The pH of this solution is 12.40, due to the presence of the strong base hydroxide ion and the weak base cyanide ion.

Procedure

Four different experiments were performed. The first experiment used solutions one and two. This experiment stepped the activity of fluoride only, from 1.0×10^{-3} to 1.0×10^{-2} for the forward activity step and then from 1.0×10^{-2} to 1.0×10^{-3} for the reverse activity step. The transient signal here would be the dynamic response of the fluoride ISE to fluoride ion. This is usually referred to simply as the dynamic response since very few studies of voltage response to interferent species have been done. Experiment two paired solutions one and three. In this case fluoride activity remained constant, while hydroxide was stepped from 1.0×10^{-6} to 7.4×10^{-2} molar in the forward step and the opposite in the reverse step. This

experiment would measure the dynamic response of the fluoride ISE to its only known static case interferent, hydroxide ion, and is reported here for the first time. This would provide a useful measure of whether the response times of the fluoride ISE to fluoride and hydroxide were comparable or not. The third experiment used solutions one and four. In this case the activities of fluoride and hydroxide were constant, while chloride and bromide ions were both stepped simultaneously. The forward step of activity was from 0 to 4.5×10^{-3} molar activity of both chloride and bromide, while the reverse step was the opposite. With this experiment, we investigate the effect of chloride and bromide ion on the dynamic response of the fluoride ISE. Experiment four used solutions one and five. In this case, the activity of fluoride ion was held constant. The hydroxide activity was stepped from 1.0×10^{-6} to 2.5×10^{-2} molar in the forward direction. Chloride and bromide were both stepped from 0 to 3.0×10^{-3} molar activity in the forward direction. And cyanide was stepped from 0 to 3.0×10^{-3} molar activity of cyanide. This experiment would measure the dynamic response of cyanide ion, if there was any response, in the presence of chloride, bromide, and hydroxide ions. The procedure for data collection of a typical experiment follows. For each experiment, the two appropriate solutions were loaded into separate solution reservoirs. Teflon tape was used to help make the polyvinyl chloride pipe threads of the reservoir have a gas tight seal. The teflon tape should be wound around the screw-cap threads, and in a spiraling fashion. The teflon tape should be wound from the bottom of the screw-cap threads to the top of the threads. The teflon tape should be drawn taught against the

threads before tightening the screw-cap, so that the screw-cap may be freely tightened without the teflon tape bunching up. If the teflon tape bunches up, it will not seal the solution reservoir properly. Also it will be difficult to remove the screw-cap after the experiment is finished. A special homemade two-handed wrench is used to tighten the screw-cap onto the reservoirs. As mentioned previously, nitrogen gas has been used to pressurize the reservoirs containing the solutions. This was done by fitting a 10 cm section of 6 mm o.d. copper tubing to the regulator, which in turn had been connected to a line of Nalgene tubing which was fixed by means of a hose clamp to the copper tubing. The Nalgene tubing was split into two lines by means of a "Y" connector of copper, and then both resulting lines of Nalgene tubing were connected to the inlet of each reservoir by means of hose clamps. The outlet of each solution reservoir is connected to another length of Nalgene tubing, which leads to a solenoid valve, and finally to a jet nozzle. After all connections are made, the solution reservoirs are charged with nitrogen to the desired pressure. The indicator and reference electrodes are then placed in the electrochemical cell and connected to the ion meter and must be positioned in that order. Care must be taken to insure that each "O" ring is placed so that a seal is obtained between the electrochemical cell body and the threaded plugs that hold the electrodes. When properly fitted, the reference electrode will fit securely in its threaded plug, with the glass frit of the end of the reference electrode about 2 mm away from the body of the indicator electrode. At this point, the electrodes should be primed with solution "A," but only if solution "A" is not expected to react harshly

with the surface of the ISE membrane. The ion meter should be taken off the standby mode of operation, and the proper functioning of the electrodes and ion meter checked. Dr. Young has developed a program for experimental control and data acquisition using the Microsoft QuickBASIC language. This program has been dubbed KINETICS.BAS and is executed next. Sample identity and experimental parameters are entered before each data acquisition. The solution temperature is entered next. KINETICS.BAS then asks for the identity of the analyte ion, its initial (solution "A") activity, and its final (solution "B") activity. KINETICS.BAS then queries for information about the interferent ions present, if there are any. The program asks for the interferent ion identity, and if no answer is given, the program skips all questions pertaining to interferents. If an interferent ion identity is given, then KINETICS.BAS follows up with questions about its initial and final activities. Then the total number of datum points to be collected is input. This quantity is the sampling rate in hertz times the duration of the signal to be recorded. KINETICS.BAS now prompts the user to turn on the 12V power supply of our own design to drive the solenoid valves. The program then asks for the digital acquisition board channel that the data will be input through. In these experiments the channel used is channel one. The digital acquisition board that we are using has a programmable analog voltage input range of 5 preset selections. The ranges are, from smallest to largest, ± 0.3125 V, ± 0.6250 V, ± 1.2500 V, ± 2.500 V, and ± 5.000 V. The analog voltage input range is selected from these values. The last parameter to be selected before data acquisition begins is the sampling rate in

hertz. KINETICS.BAS asks that a key be pressed to initiate the data collection subroutine. Upon the key press the solenoid valve "A" is opened and the sampling of the voltage of the electrodes (as output from the ion meter) begins. A flow of solution "A" is sprayed rapidly onto the surface of the ISE, with the reference electrode being downstream of the ISE. The data are collected and stored in a temporary manner, the purpose being to see if the voltage of the electrodes has stabilized. Once the voltage of the electrode pair has stabilized, then 100 (permanent) lead-in datum points are collected and the flow of solution "A" is shut off and solution "B" turned on. This creates the rapid forward activity step at the surface of the ISE. The user-specified number of datum points is collected at the user-specified sampling rate, and KINETICS.BAS asks what file number the data are to be stored as. If the number input is N, then the data file is named IKIN_N. The data file IKIN_N is then stored to the microcomputer hard disk. All the while solution "B" is flowing, and "A" is off. After a second key press, the solenoid valves are toggled once again to create the reverse activity step. Thus a second group of 100 lead-in datum points is collected, the flow of solution "A" turned on, and the flow of solution "B" turned off. After the previously specified number of datum points is collected, the reverse activity step data file is stored on the hard disk and is named IKIN_N+1. After the reverse activity step the data are stored to the hard disk, and the flow of solution "A" is turned off. This completes one cycle of a forward activity step followed by a reverse activity step, with two separate data files consecutively numbered having been created with the user specified number of datum points and

sampling rate. KINETICS.BAS returns the operator to its main menu at this point. In this manner it is possible to collect many series of forward and reverse activity steps for a given pair of analyte solutions and ISE.

Results and Discussion

Fluoride Activity Steps

A total of 16 forward and 16 reverse activity steps have been collected using fluoride solutions one and two. Of these, 12 cycles were collected at very high resolution (10000 Hz) for 1 second duration, and the remaining four cycles were collected at low resolution (100 Hz) for 10 seconds. The files have been named IKIN 42XX. The files are in three distinct groups. Files IKIN 4201 through 4208 used the programmable analog voltage input range of ± 0.6250 volts, with 10000 datum points collected at 10000 Hz. Files IKIN 4209 through 4224 used the programmable analog voltage input range of ± 0.3125 volts, with 10000 datum points collected at a sampling rate of 10000 Hz. The lower analog voltage input range of files IKIN 4209 through 4224 resulted in a slightly higher resolution of the electrode voltage, without exceeding the limits of the input range. Finally, files IKIN 4231 through 4238 used the same analog voltage input range, but collected 1000 voltage samples at a 100 Hz sampling rate. A few generalized statements can be made regarding the groups of data collected. All electrograms were of exceptionally high quality, and can later have curves fitted to them using a nonlinear regression routine. The voltage resolution in all cases was limited by the natural fluctuations

in the electrode voltage and not by the digital acquisition board's digitizing resolution. The time resolution of the converging wall-jet instrument captured many details that would not have been seen using an instrument of lower time resolving power. The very high sampling rate files can show enhanced detail that would not have been seen at a lower sampling rate. Both the forward and reverse activity steps all showed rapid responses, and the change in voltage followed that predicted by the Nernst equation. The resultant lineshapes must be due to either activity steps in fluoride or nitrate ion, as these are the only species in these two solutions whose activities have changed. However, since the relative change in nitrate activity is minute in comparison to the tenfold change in activity of fluoride ion, the resultant lineshapes can be assumed to be caused by the activity of fluoride alone.

High (time) resolution forward activity steps. A representative very high time resolution forward activity step is given in Figure 3-1, and its companion reverse activity step is given in Figure 3-2. Figure 3-1 is a plot of file IKIN 4213, while Figure 3-2 is a plot of data file IKIN 4214. The forward activity step shown in Figure 3-1 shows a change of voltage of -64 millivolts, and reaches its full change in voltage in about 240 milliseconds. The voltage change is somewhat larger in magnitude than the -59.2 millivolts predicted from the Nernst equation, but not drastically so, and is within an acceptable experimental uncertainty. The forward response time for the full change in voltage, t_{100} , is approximately 240 milliseconds, and represents both the capability of the converging wall-jet instrument to create very rapid activity steps and the short response time of the lanthanum fluoride based fluoride ISE.

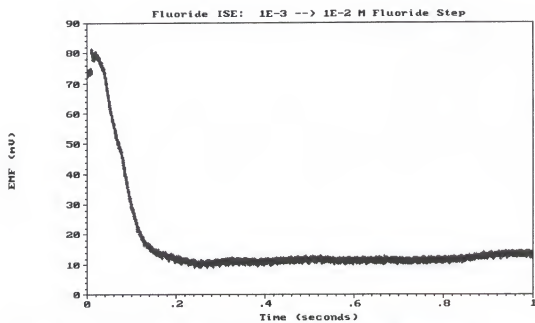


Figure 3-1. Forward fluoride activity step at very high resolution.

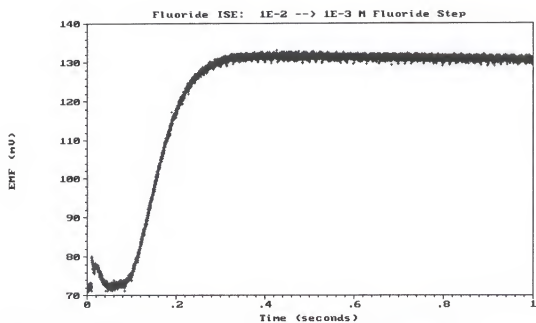


Figure 3-2. Reverse fluoride activity step at very high resolution.

Mertens et al. found forward response times (t_{90}) of 100 milliseconds, 2.5 seconds, and 13 seconds for three different fluoride ISEs using a concentration step of 1×10^{-3} M fluoride to 1×10^{-2} M fluoride.⁶ They used an instrument that was capable of measuring true dynamic responses. Our response time measurements (t_{100}) using only one electrode are comparable to response time measurements (t_{90}) of their fastest electrode, and an order of magnitude or more faster than their slowest electrodes. All other parameters and performance being equal, t_{100} response times will be longer by necessity than t_{90} response times. At a later date we will fit theoretical curves to our data to find t_{90} values for direct comparison to the value reported by Mertens et al. Frenzel and Bratter used an FIA instrument to measure the response time of a fluoride ISE to fluoride activity steps.⁴³ They did not use solution activities that directly compare to ours, but for a twofold increase in fluoride activity (2.63×10^{-3} M to 5.26×10^{-3} M) they found t_{95} to be 5.92 seconds. This larger response time could reflect the lesser capability of an FIA instrument to create ideal activity steps compared to a wall-jet instrument, or it could reflect a poorly functioning fluoride electrode. Van Oort and Van Eerd used a flow cell instrument to measure the forward response time of the fluoride ISE to increases in fluoride concentration.³¹ For a step from 1×10^{-3} M fluoride to 1×10^{-2} M fluoride, they found t_{63} to be 6 seconds for an unpolished fluoride ISE and 10 seconds for a polished fluoride ISE. Once again, the slow response times could be attributed to the limitations of a flow cell instrument in creating ideal activity steps, or a poorly functioning electrode. The fastest dynamic responses reported for the fluoride ISE

have been found using instruments capable of creating very fast activity steps in fluoride. Those instruments using flow cells and FIA instruments have found response times at least an order of magnitude larger than the wall-jet instruments. This evidence suggests that the shorter response times measured by the wall-jet instruments are due to the more instantaneous creation of activity steps in wall-jet instruments, and not due to poorly functioning electrodes in the flow cell and FIA instruments. Referring back to Figure 3-1, four distinct regions can be seen. The first region of the voltage/time curve is the voltage due to fluoride solution one, which had a fluoride activity of 1.0×10^{-3} M fluoride. This region lasts for 10 milliseconds (100 lead-in datum points at a sampling rate of 10000 Hz). However, the voltage prior to these 100 lead-in datum points had met our voltage stability criterion. At this point, fluoride solution one is switched off while simultaneously fluoride solution two (1.0×10^{-2} M activity fluoride) is switched on. It is at this point that the second region in the voltage/time curve is seen. This is a voltage spike of about 5 millivolts positive. The voltage spike is probably due to electronic noise in our instrument, but despite experiments to determine its source, it could not be isolated and corrected. This voltage spike is present in all voltage versus time data that we have collected, and is always in the positive direction. After the voltage spike, the transition region begins, and it is here that the electrode begins to respond to fluoride solution two. The shape of the transition region appears to be an exponential, hyperbolic, or square root function. These lineshapes are typical of the transition region.^{1,2} The exact function will be revealed when the data are

fitted to such lineshapes. The last distinct region begins at about 240 milliseconds, and is a relatively slowly drifting response towards higher voltages. It is not easy to discern this region in the data files of 1 second duration, but it can easily be seen in the data files of 10 seconds duration presented later.

High (time) resolution reverse activity steps. In Figure 3-2, the reverse activity step immediately following the data shown in Figure 3-1 is plotted. These data are file IKIN 4214. Here the voltage change is approximately 60 millivolts, and agrees well with the expected 59.2 millivolts predicted from the Nernst equation. The reverse response time is rapid, with t_{100} being approximately 350 milliseconds. It is a characteristic of ISE dynamic response to have reverse response times about twice those of forward response times for any given ISE and pair of analyte solutions, and the reason for this remains unclear.^{1,2,36,51,52} In our case, the reverse response time is not twice as large, but about 50% greater than the forward response time, but is still within the general doubling of the response time. Mertens et al. found the reverse response times (t_{90}) to be 190 milliseconds, 10 seconds, and 37 seconds for three different fluoride ISEs following a concentration change of 1×10^{-2} to 1×10^{-3} molar fluoride.⁶ Our reverse response time (t_{100}) of 350 milliseconds compares to their fastest electrode. Frenzel and Bratter did not measure a reverse response time for solutions of similar fluoride activities to what we have used, but all reverse response times that they have measured were greater than 7 seconds.⁴³ Van Oort and Van Eerd found a reverse response time (t_{63}) of 16 seconds for an unpolished and 21 seconds for a polished fluoride electrode

following a change in concentration of 1×10^{-2} to 1×10^{-3} molar fluoride.³¹ As was the case with the forward response time, the reverse response time is very short for the wall-jet instruments, and is an order of magnitude smaller than that reported for the flow cell instrument. Again, this is probably attributed to the superior capability of wall-jet instruments to create nearly ideal activity steps. The same four distinct regions seen in the forward activity step are seen in the reverse activity step. The voltage spike is positive in both the forward and reverse activity steps, while the transition region is decreasing in the forward and increasing in the reverse activity steps. Also, the slowly drifting response is in opposite directions for the forward and reverse activity steps. The transition region is symmetric in shape regarding the two directions of activity change. Upon comparing the forward and reverse activity steps, the symmetry of the pair suggests that all processes happening in the forward step are electrochemically reversible and of approximately the same time frame in the reverse activity step.

Low (time) resolution forward activity steps. Figure 3-3 and Figure 3-4 show the fluoride ISE response following a forward (Figure 3-3) and reverse (Figure 3-4) activity step using fluoride solutions one and two, but here the sampling rate is low (100 Hz) while the duration is long (10 seconds). The forward activity step data file plotted in Figure 3-3 is IKIN 4231, while the companion reverse activity step shown in Figure 3-4 is IKIN 4232. In these two figures, the activity step creation occurs beginning at 1 second (100 lead-in datum points at a 100 Hz sampling rate). The change in voltage for Figure 3-3 is -65 millivolts while the forward response time

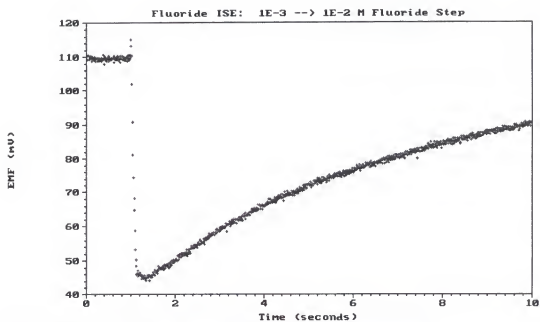


Figure 3-3. Forward fluoride activity step at low resolution.

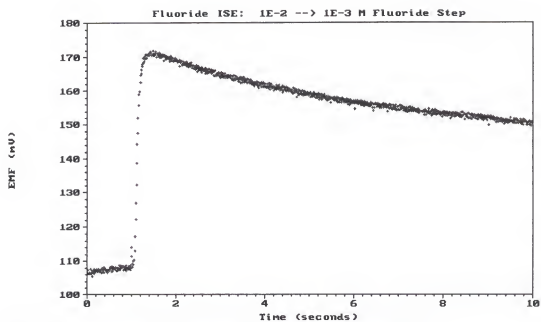


Figure 3-4. Reverse fluoride activity step at low resolution.

(t_{100}) is approximately 300 milliseconds. These parameters are comparable to the results we obtained for forward activity steps using the 10000 Hz sampling rate. No different behavior is seen upon comparing the low (Figure 3-3) and high sampling rate (Figure 3-1) forward steps. It is clear that a slowly drifting response towards more positive voltages is present as the fourth region of Figure 3-3. This behavior could not clearly be discerned by Figure 3-1 alone.

Low (time) resolution reverse activity steps. Figure 3-4 shows the companion low sampling rate (100 Hz) reverse activity step. The change in voltage in this case is approximately 63 millivolts, while the reverse response time (t_{100}) is about 400 milliseconds. There is no disagreement of the results obtained for these parameters between the low and high sampling rate reverse steps. Comparing the low (Figure 3-4) and high sampling rate (Figure 3-2) reverse steps, the region of slowly drifting response can easily be seen in Figure 3-4. Comparing Figure 3-3 to Figure 3-4, one finds the same general trends that were found in comparing Figure 3-1 to Figure 3-2, and the same conclusions can be drawn. It is interesting to note that the slowly drifting region in the forward step (Figure 3-3) is symmetric to the slowly drifting region in the reverse step (Figure 3-4), while the former drifts faster than the latter. The values for the rate of drift are 5.0 and 2.4 millivolts per second for the forward and reverse steps, and both of these values are much higher than the 8 millivolts per minute reported by Frenzel.⁵⁴ This high rate of drifting response has not been reported for the fluoride ISE responding to fluoride in any of the literature, and may be caused by the high solution flow rates used in our instrument. The

symmetry of the drifting region suggests a similar and electrochemically reversible process taking place in the forward and reverse directions. The disparity in slope of the drift region suggests a difference in the kinetics of the process causing it. Given the high flow rates of the solutions used, dissolution of the membrane may account for the drifting response.

General trends in the forward steps. As was stated earlier, many forward and reverse steps have been collected. For the low sampling rate experiments, the resulting lineshapes all showed the same general features. For the high sampling rate experiments, many of the forward step voltage/time responses showed two distinct regions within the transition region. The first region was a rapidly decreasing curve, while the second region was a moderately decreasing curve. The reason for two distinct slopes within the transition region may be that the electrode had never been used before, and was sluggish to respond to high activities of fluoride. For the best four high sampling rate forward steps (IKIN 4201, 4205, 4207 and 4213), the average change in voltage was -57 millivolts, and the range was -51 to -64 millivolts. While the average change in voltage is Nernstian, the range of voltage changes shows moderate experimental error. The average t_{100} for the same four high sampling rate data files was 240 milliseconds, and the range was 200 to 280 milliseconds, again showing moderate experimental uncertainty.

General trends in the reverse steps. All reverse steps at high sampling rates showed the same features as Figure 3-2. Using all 12 data files, the average change in voltage was 60 millivolts and the range of values obtained was 57 to 61

millivolts. This group shows Nernstian response and little experimental error. The average reverse response time was 360 milliseconds, while the range was 340 to 420 milliseconds. The experimental error in this group is much less than for the forward steps. The reason may be that the new electrode was more able to stabilize quickly to lower activities of fluoride.

Hydroxide Activity Steps

No previous dynamic response studies of hydroxide activity steps using a fluoride ISE have been reported. Sixteen forward and 16 reverse hydroxide activity steps have been collected using fluoride solutions one and three. Of these, eight cycles were collected at very high resolution (10000 Hz) for 1 second duration (IKIN 4301-4316), four cycles were collected at low resolution (100 Hz) for 10 seconds (IKIN 4321-4328), and four cycles were collected at low resolution (100 Hz) for 20 seconds (IKIN 4331-4338). All have used the programmable analog voltage input range of ± 1.2500 volts. The higher voltage input range was necessary because all of these electrograms showed large voltage changes. Some generalized statements can be made regarding the groups of data collected. Although these electrograms are of lower quality than the fluoride (only) activity steps, the signal to noise ratio is sufficient to permit curves fitted to them using a nonlinear regression routine. However, since the lineshapes within the first 250 milliseconds of the electrograms are complex, the use of a curve fitting routine in this region seems to be of questionable value. Curve fitting will be possible for the drift region that

begins after about 250 milliseconds. Compared to the electrograms of the fluoride steps, the voltage resolution is much less. Digitization noise manifests itself in these electrograms, and will be a source of error in any fitted curves. The time resolution of the converging wall-jet instrument has captured many details in the electrograms that would not have been seen using an instrument of lower time resolution. Nor would such an instrument have created an activity step fast enough to cause such complicated behavior in the resulting voltage response. The very high sampling rate files clearly show enhanced detail that is not seen in the low sampling rate files. Both the forward and reverse activity steps all showed rapid initial responses, followed by a slower voltage drift of considerable magnitude. In general, the voltage responses are not Nernstian. Files IKIN 4321-4328 will not be discussed, as files IKIN 4331-4338 show the same general behavior, but the duration of sampling was twice as long for the latter group. In these two solutions, only the activities of hydroxide, hydronium, and nitrate have changed. A change in hydroxide ion necessarily causes a change in hydronium ion in aqueous solutions, so when one speaks of an activity change in one of these ions, one is of necessity speaking of an activity change in both of them. As was the case with the fluoride only activity steps, the change in the ion of interest (a seven-fold change in hydroxide activity in this case) overshadows the minute relative changes in the activity of the nitrate ion. Thus it can be said with confidence that the effects shown in the paragraphs to follow are due to the hydroxide/hydronium ion activity changes, and not due to nitrate.

High (time) resolution forward hydroxide activity steps. A representative very high time resolution (10000 Hz) forward hydroxide activity step is given in Figure 3-5, and its companion reverse activity step is shown in Figure 3-6. Figure 3-5 is a graph of data file IKIN 4301, while Figure 3-6 represents file IKIN 4302. The forward hydroxide activity step shown in Figure 3-5 shows several regions. First, there is a stable response to fluoride solution one, occurring for the first 10 milliseconds. Next, the previously mentioned voltage spike occurs. After this, the electrode begins to respond to fluoride solution three. There is a decrease in the initial voltage by approximately -33 millivolts taking place within 40 milliseconds after the change of solutions. This is followed by another decrease in voltage of approximately -26 millivolts (compared to the initial voltage) occurring 70 milliseconds after the change in solutions. The time frame of this region (170 milliseconds) is about the same time frame as the fluoride ISE responding to activity steps in fluoride (240 milliseconds, shown in Figure 3-1). The last region is a large and rapid drift towards higher voltages, and begins at about 170 milliseconds. The voltage never stabilizes within the first second. The static selectivity coefficient for hydroxide is 0.10. Fluoride solution three has hydroxide equal to 7.4×10^{-2} M activity, and so the equivalent fluoride activity is 7.4×10^{-3} M. The Nicolsky equation predicts a voltage change of -51.5 millivolts. Both of the voltage minima reflect a change in voltage well below that which is predicted by the Nicolsky equation. The voltage change is only 58 percent of that expected from a Nernstian voltage change, using a value of -30 millivolts for the average of the two minima seen.

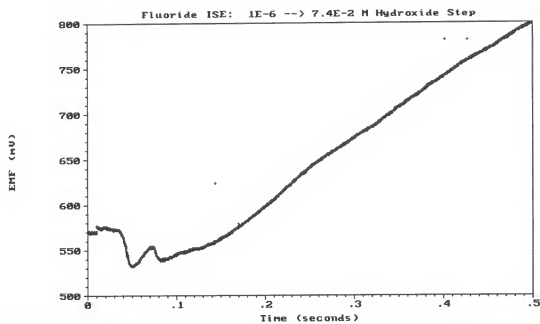


Figure 3-5. Forward hydroxide activity step at very high resolution.

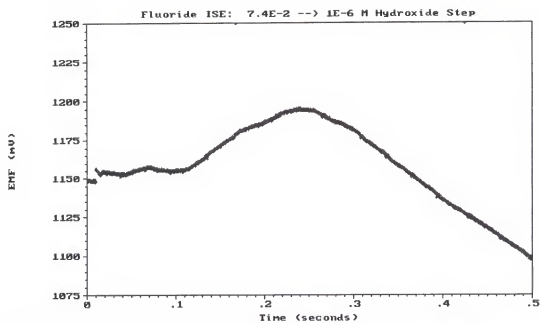


Figure 3-6. Reverse hydroxide activity step at very high resolution.

High (time) resolution reverse hydroxide activity steps. The reverse hydroxide activity step immediately following the data shown in Figure 3-5 is plotted as Figure 3-6 (IKIN 4302). The reverse hydroxide activity step also shows several regions. The first region lasts for 10 milliseconds and is a stable response to fluoride solution three. The voltage spike region occurs next. Then the electrode begins to respond to fluoride solution one. There is a increase in the initial voltage by approximately 8.0 millivolts taking place within 60 milliseconds after the change of solutions. Another increase in voltage of approximately 46 millivolts (compared to the initial voltage) occurs 240 milliseconds after the change in solutions. The final region is a large and rapid drift towards lower voltages, beginning at about 300 milliseconds. Again, the voltage never stabilizes within the first second of the electrode's response. In this case, the Nicolsky equation predicts a voltage change of 54.8 millivolts. The first voltage maximum reflects a change in voltage well below that which is predicted by the Nicolsky equation. The second voltage maximum reflects a change in voltage that could be considered Nernstian. There are two voltage minima in the forward step response, and two voltage maxima in the reverse step. There seems to be no correlation between forward and reverse step voltage changes. There is, however, a correlation between forward and reverse step response times. The first minimum of the forward step occurs at 40 milliseconds after the change in solutions, while the first maximum of the reverse step occurs 60 milliseconds after the change in solutions. The second minimum of the forward step occurs 70 milliseconds after the switching of the solutions, and in

the reverse step, the second maximum occurs 240 milliseconds after the solution change. As was the case with the fluoride (only) activity steps, the kinetics of the processes taking place in the hydroxide steps are faster in the forward direction, and thus the forward response time is only about half that of the reverse. There is some symmetry in shape regarding the two directions of activity change. The near symmetry of the pair suggests that the processes happening in the forward step are also taking place in the reverse step. Since the magnitude of the voltage changes are different, this suggests that the processes are only somewhat electrochemically reversible.

Low (time) resolution forward hydroxide activity steps. Figures 3-7 and 3-8 plot the fluoride ISE response following a forward (Figure 3-7) and reverse (Figure 3-8) hydroxide activity step using fluoride solutions one and three. Here the sampling rate is low (100 Hz) while the duration of sampling is long (20 seconds). The forward activity step data file plotted in Figure 3-7 is IKIN 4333, and its companion reverse activity step shown in Figure 3-8 is IKIN 4334. In these two figures, the activity step creation begins at 1 second. The same non-monotonic behavior shown in the other hydroxide steps is present in these data also, but is more difficult to see, and considerable time resolution is lost. The two minima shown in Figure 3-5 appear as a single minimum in Figure 3-7, while the two maxima in Figure 3-6 appear as a single maximum in Figure 3-8. The extent of the drift region can clearly be seen in Figures 3-7 and 3-8. Figure 3-7 shows three regions. There is an initial voltage lasting 1 second due to fluoride solution one.

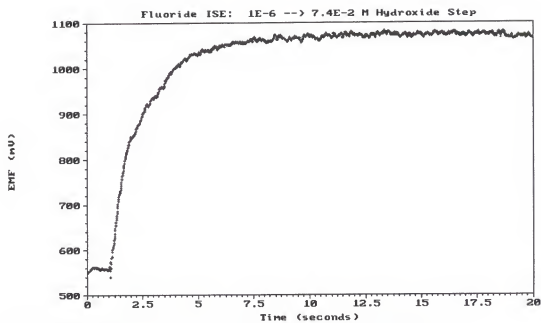


Figure 3-7. Forward hydroxide activity step at low resolution.

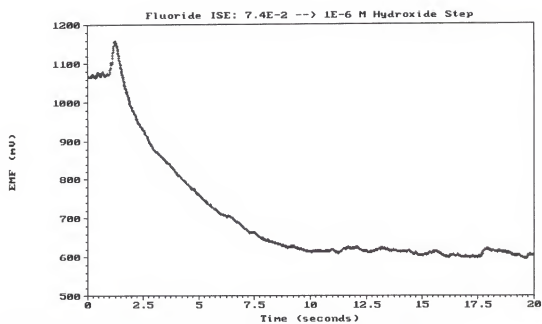


Figure 3-8. Reverse hydroxide activity step at low resolution.

The voltage spike cannot be seen because of the low sampling rate. The solutions are switched, and the voltage decreases by about 22 millivolts, below the voltage change predicted by the Nicolsky equation. Then a voltage drift towards higher voltages of about 520 millivolts occurs, and stabilizes within 9.4 seconds after the change in solutions. It appears that the drift region may be represented by an exponential lineshape.

Low (time) resolution reverse hydroxide activity steps. In Figure 3-8, the reverse hydroxide activity step is shown. The reverse hydroxide step shows the same three regions as the forward hydroxide step. The initial voltage of the electrode responding to fluoride solution three lasts for 1 second. At this point, the solutions are switched and a voltage increase of about 84 millivolts follows. This voltage change is higher than the 54.8 millivolts predicted by the Nicolsky equation. Again, the voltage spike cannot be seen. Then a drift to lower voltages occurs. The drift is about 473 millivolts towards lower voltages, and has stabilized within about 15.6 seconds after the switching of the solutions. Again, it seems that the drift region could be fitted by an exponential curve.

Comparison of the high and low (time) resolution forward hydroxide activity steps. The only different behavior seen upon comparing the low (Figure 3-7) and high sampling rate (Figure 3-5) forward steps is that the drift region is revealed in its entirety, the two minima appear as one, and the voltage change leading to the minimum is smaller for the low resolution activity step (22 millivolts) than for the high resolution activity step (33 millivolts).

Comparison of the high and low (time) resolution reverse hydroxide activity steps. Figure 3-8 shows the companion low sampling rate (100 Hz) reverse activity step. The same trends continue when comparing the low (Figure 3-8) and high sampling rate (Figure 3-6) reverse steps, except that the voltage change leading to the maximum in the low resolution activity step (84 millivolts) is larger than for the high resolution activity step (46 millivolts).

Comparison of forward and reverse hydroxide activity steps. Comparing Figure 3-7 to Figure 3-8, one can see that the kinetics of the processes causing the drift are faster for the forward hydroxide activity step. The drift stabilizes within 9.4 seconds after the switch in solutions for the forward hydroxide activity step, while it takes 15.6 seconds for the reverse activity step. The magnitude of the drift is slightly larger in the forward hydroxide activity step (520 millivolts) versus the reverse hydroxide activity step (470 millivolts). Also, the change in voltage leading to the voltage minimum for the forward hydroxide activity step (22 millivolts) is much smaller than the change in voltage leading to the voltage maximum in the reverse hydroxide activity step (84 millivolts). The kinetics of the processes taking place in the forward steps are faster than for the reverse steps, and like the fluoride only activity steps, lead to a response time for the reverse steps being longer by a factor of two in general. Due to the general symmetry of the forward and reverse steps, it seems likely that the same processes are taking place, but in opposite directions. The voltage changes leading to the minima in the forward steps are smaller than those leading to the maxima for the reverse steps. In the case of higher numbered

data files, (which were collected after many previous forward and reverse cycles), the voltage change gap is even greater. Thus it seems that a fast, but somewhat electrochemically irreversible process is causing this behavior. The voltage change during the drift region is larger for the forward step than the reverse step, but only slightly so. The symmetry of the drifting region, coupled with the fact that the voltage drift is of similar magnitude, suggests a similar and electrochemically reversible process taking place that is sluggish in the forward and reverse directions.

Figures of merit for the group of forward and reverse hydroxide activity steps.

Data from many forward and reverse hydroxide activity steps have been collected. For the low sampling rate experiments, the resulting lineshapes all showed the same non-monotonic behavior. Considering the group of low resolution forward steps, the average time needed for the drift to become stable was 11.0 seconds, the average drift was 578 millivolts, and the average change in voltage leading to the voltage minimum was 27 millivolts. For the group of low resolution reverse steps, the average time for the drift to become stabilized was 14.3 seconds, its average magnitude was 472 millivolts, and the average change in voltage leading to the voltage maximum was 90 millivolts. All of the lineshapes were reproducible in the high resolution data file group as well. All of them have either two minima or two maxima, followed by considerable drift. For the forward activity steps, the average time for the first and second minima were 41 and 66 milliseconds after the switching of the solutions, and these times showed great precision. Their change in voltages

averaged 33 and 22 millivolts respectively, but these voltages were not very reproducible. The range of values for the first minimum was from 15 to 48 millivolts, and for the second, 5.0 to 40 millivolts. For the reverse steps, the average time for the first and second maxima were 59 and 230 milliseconds, and these times were also precise. The corresponding average voltage changes were 10 millivolts for the first maximum and 54 millivolts for the second maximum. The reproducibility of the voltage changes was better, with a range of 10 to 13 millivolts for the first maximum and 46 to 61 millivolts for the second.

Chloride-Bromide Activity Steps

As with the previously mentioned experiments done in our laboratory, many cycles of forward and reverse chloride-bromide steps have been performed. Seventeen forward and 17 reverse chloride-bromide activity steps were collected using fluoride solutions one and four. The first nine cycles were collected at very high resolution (10000 Hz) for 1 second duration (IKIN 4401-4418), four cycles were collected at low resolution (100 Hz) for 10 seconds (IKIN 4421-4428), and four cycles were collected at low resolution (100 Hz) for 20 seconds (IKIN 4431-4438). All but the first cycle used the programmable analog voltage input range of ± 0.3125 volts, and the first cycle used ± 0.6250 volts. The smaller voltage input range was used after the first cycle because the peak to peak voltages observed fit within the smaller range, allowing better voltage resolution. Some generalized statements can be made regarding the groups of data collected. These electrograms are of a

quality comparable to the fluoride (only) activity steps, and the signal to noise ratio is sufficient to permit curves fitted to them using a nonlinear regression algorithm. At this time there has been no theory which has been advanced to explain the behavior of ISEs responding to changes in ion activities which are not static case interferent species, as too few studies have been performed. Therefore, we have no model for which to compare our experimental results with theoretical ones. Curve fitting, however, will be possible for both the forward and reverse steps. The voltage resolution is about that which was seen in the fluoride (only) steps. All forward steps showed a rapid shift to lower voltages, followed by a slower drift towards higher voltages. All reverse steps showed a slow drift towards higher voltages. Since chloride and bromide are not static case interferents, and therefore have no selectivity coefficient, one cannot comment as to whether a Nernstian change of voltage has occurred or not for these experiments. Files IKIN 4401-4428 will not be discussed, as files IKIN 4431-4438 show the same general behavior, but the duration of sampling was much longer for the latter group. In these activity steps, chloride and bromide have been stepped in their activities, as well as sodium, potassium, and nitrate. Chloride and bromide have each been stepped from zero to 4.5×10^{-3} M activity, increasing for forward steps. The step in sodium is from zero activity in solution one to 9.0×10^{-3} M activity in solution four. The change in potassium is decreasing for forward steps, and is minute in comparison to the other activity changes. The same is true for nitrate. Thus, in the following paragraphs describing our chloride-bromide results, the effects seen could be caused by

chloride, bromide, and/or sodium ion. At the time that these solutions were prepared, we had not seen the literature that described the effects that very large sodium activity steps are reputed to have ⁴³ on the fluoride ISE, and other static case non-interferent cations. The solutions were prepared using sodium fluoride and sodium bromide as the reagents for the sources of chloride and bromide respectively. We had not at that time known or suspected that sodium could effect the lineshapes of the resulting chloride-bromide activity steps, and we were interested in a study of the effects of the various halides and cyanide on the halide electrodes and the iodide/cyanide electrode. The following results of our chloride-bromide activity steps could then be due to activity steps in chloride and/or bromide and/or sodium.

Frenzel and Bratter's experiments with the fluoride ISE and chloride salts.

Frenzel and Bratter ⁴³ used an FIA instrument to study the effects of chloride on the dynamic response of the fluoride ISE, but no previous studies of the effect of bromide on the dynamic response of the fluoride ISE have been reported. Frenzel and Bratter examined the time response and voltage change behavior of fluoride solutions with varying sample viscosity, ionic strength, pH, and complexing ions. The complexing ions they examined were Ca^{++} , Mg^{++} , Si^{4+} , Fe^{+++} , and Al^{+++} , species that were not examined in our work. However, in their experiments involving ionic strength effects, they used some chloride containing salts. It is well known that if activities are to be determined with ISEs rather than concentrations, analyte ionic strength must be held constant between samples and standards. Frenzel and

Bratter looked at what effects violating this maxim would have on the time and voltage response curves of the fluoride ISE. They performed experiments that stepped both fluoride activity and ionic strength. They performed experiments that had constant fluoride concentration, but variable total ionic strength. And they performed experiments with constant total ionic strength using different salts, and with a fluoride activity step, and compared the time response and voltage curves obtained. In general, solutions of higher ionic strength showed lower fluoride activities, but this is due in part to the uncommon ion effect. More importantly, for activity steps of fluoride with total ionic strength not held constant, differences in the time response and voltage change were noted, as well as transient peaks. A doubling of the response time, a 20% smaller change in voltage, and transient peaks towards higher voltages were shown for a solution change from 100 micrograms per liter fluoride to 500 micrograms per liter fluoride in 1.0 molar sodium chloride. Thus, the effect of the total ionic strength of the solutions used can be quite large for both the voltage change and the response time observed. In the experiments performed at constant fluoride concentration but changing ionic strength, positive and negative transient peaks were seen. When the solution with higher total ionic strength flowed onto the ISE, a voltage increase of about 5 millivolts was seen, lasting for about 30 seconds. The 5 millivolt excursion was beyond the change in voltage for the fluoride activity change due to the increasing ionic strength (and therefore slightly decreasing fluoride activity), which was about 1 to 2 millivolts. Therefore the excursion of 5 millivolts must have been due to the

species used to increase the total ionic strength, or species used in the carrier solution's total ionic strength adjustment buffer, but unfortunately both compositions were unspecified. A negative transient of about 3 millivolts, lasting for about 30 seconds, was seen upon a change back to the initial solution, and again the excursion was beyond that of the voltage change due to the total ionic strength changing. Lastly, they performed experiments where the fluoride activity was stepped and total ionic strength was held constant, but using different salts to perform the change in ionic strength. In these experiments, the composition of the salt effected the magnitude of the change in voltage seen, and also caused non-monotonic behavior, with transients leading to higher voltages for forward steps. No mention of the effect on the response time was given for this group of experiments. They chose NaCl, NaNO₃, KNO₃, KCl, CaCl₂, and MgCl₂ as the salts used to hold the total ionic strength constant for these solutions. The first four salts are of the greatest interest to our study. The sodium salts showed larger effects than did the potassium salts. Sodium nitrate and sodium chloride showed about the same magnitude of voltage change reduction and transient peak generation. Potassium nitrate showed a slightly larger voltage change reduction than did potassium chloride. Calcium chloride had about the same magnitude of effects as the potassium salts. Magnesium chloride had the greatest effects, but this is not surprising, given magnesium ion's ability to form complex ions with fluoride. Thus it seems that the cation used effected the results more than the anion used, although both cations and anions did effect the results. The caveat here is that

Frenzel and Bratter did not give the exact compositions of the solutions used in these last experiments, only giving the initial and final fluoride activities, the activity and type of added salt used to change the composition of the ionic strength buffer, and the fact that a total ionic strength buffer (of unspecified chemical composition) was used to hold the total ionic strength constant. Without these specifics, they may have come to improper conclusions with respect to the relative importance of the various ions used in altering the electrode response, because the sodium, potassium, chloride and other ions that were used to spike the solutions may have had less of an effect than the decreased activity (or removal) of the species in the total ionic strength buffer itself. Frenzel and Bratter did not perform any experiments using bromide salts. Nor did they perform any experiments using the general conditions of our own. In our experiment, we have held total ionic strength and fluoride activity constant, but have changed the salts used to make the solution have a high and constant total ionic strength. In this manner, we have effectively performed a step in chloride and bromide ion. This was of interest in the detection of hydrogen halide gases in fire extinguishing studies. But our study follows to some degree the constant ionic strength experiment of Frenzel and Bratter, but without a simultaneous activity step of fluoride.

Low (time) resolution forward chloride-bromide activity steps. A representative low resolution (100 Hz) forward chloride-bromide activity step is shown in Figure 3-9, and its companion reverse activity step is shown in Figure 3-10. Figure 3-9 is a graph of data file IKIN 4437, while Figure 3-10 represents file

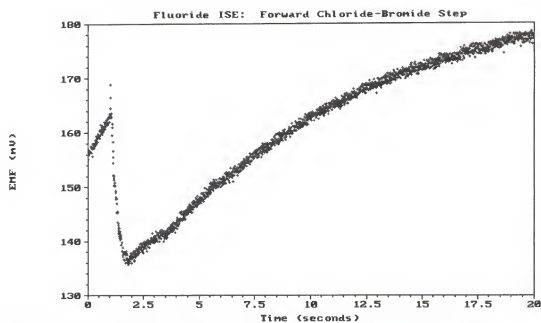


Figure 3-9. Forward chloride-bromide activity step at low resolution.

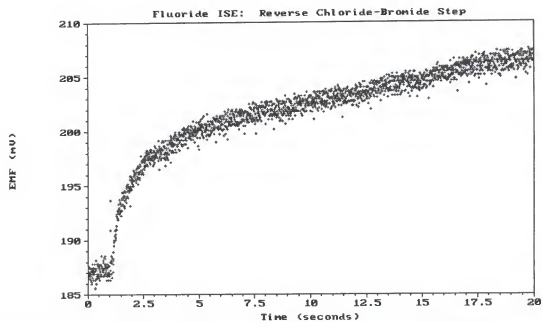


Figure 3-10. Reverse chloride-bromide activity step at low resolution.

IKIN 4438. The forward chloride-bromide activity step shown in Figure 3-9 shows three main regions. First, there is a slowly drifting response to fluoride solution one, occurring for the first second. After this, the electrode begins to respond to fluoride solution four. There is a moderately rapid decrease in the initial voltage by approximately -27 millivolts taking place after the change of solutions. This second region lasts for some 700 milliseconds, and the response time is about an order of magnitude longer than for either the fluoride steps (Figure 3-1) or the hydroxide steps (Figure 3-5). The last region is a slow drift towards higher voltages, and begins about 1 second after the change in solutions. The voltage never stabilizes within the first 20 seconds.

Low (time) resolution reverse chloride-bromide activity steps. The reverse chloride-bromide activity step immediately following the data shown in Figure 3-9 is plotted as Figure 3-10 (IKIN 4438). The reverse step shows three main regions. The first region lasts for 1 second and is a slowly drifting response to fluoride solution four. The second region is a rapid drift towards higher voltages, and lasts for about 2 seconds after the change of solutions. The change in voltage of this region is approximately $+12$ millivolts, somewhat smaller than the change in voltage of the second region in the forward steps. The third region is a continuing drift towards higher voltages, but at a slower rate, lasting for the duration of the datum sampling.

Comparison of forward and reverse chloride-bromide activity steps. As was the case with the fluoride (only) activity steps, the kinetics of the processes taking

place in the middle region of the chloride-bromide steps are faster in the forward direction than the reverse. The response time for the overshoot is longer in the reverse steps by about a factor of two. The middle region shifts towards lower voltages in the forward steps, and towards higher voltages in the reverse steps, indicating that this region may represent the forward and reverse reaction(s) of the same chemical reaction(s). The slowly drifting regions of both the forward and reverse steps are towards higher voltages only, and thus probably represent reactions of the same type and direction, but do differ in their kinetic rates.

Comparison of both laboratories' results. In the case of Frenzel and Bratter's results, their forward step of chloride caused a sharp 5 millivolt increase in voltage, which was followed by an incomplete relaxation towards the initial (solution one) voltage, due to the slight change in fluoride activity.⁴³ Their results showed no drift regions, and a much longer time-frame for both the discontinuous voltage increase and the relaxation region that followed than our results did. The disparity between the direction of the voltage change must be due to the compositions of the solutions used. In their case, they have performed a increasing step of sodium and chloride of unspecified activity in a solution of total ionic strength equal to 0.50 M activity, while simultaneously performing a decreasing step of other ions used to buffer the ionic strength of their fluoride solution. In our case, we have performed an increasing step of sodium, chloride, and bromide, with no other ionic species activities stepped, and using potassium nitrate to buffer the total ionic strength at 0.100 M activity. The same argument can be made to explain the difference in the

directions of the voltage changes for the reverse chloride-bromide steps. In both sets of experiments, there are too many degrees of freedom to state exactly what effect any singular ion has as far as the direction of voltage change is concerned. However, it is clear that non-static case non-interferent ions, like potassium, sodium, chloride, and bromide may effect the response time and voltage changes of fluoride activity steps with the fluoride ISE. Comparing the results of Frenzel and Bratter to our results, their results have smaller and slower voltage changes. The smaller voltage changes are probably due to both the differences in solution compositions used and the less ideal creation of activity steps in their FIA instrument. The slower voltage changes are probably due less to the differences in the solution compositions used than the creation of faster and more ideal activity steps in our converging wall-jet instrument. As a result of our experiments, there is the possibility that chloride and/or bromide may cause minor interference in the determination of fluoride using a fluoride ISE for monitoring hydrogen halide content in fire extinguishing studies, however the possible effects of sodium ion cannot be excluded.

Four-ion Activity Steps

No dynamic response studies of activity steps involving cyanide ion using a fluoride ISE have appeared previously in the literature. In these experiments with cyanide and the fluoride ISE that we report here, 16 cycles of forward and reverse activity steps have been collected using fluoride solutions one and five. Following

the pattern of the experiments reported earlier in this dissertation, eight cycles were collected at very high resolution (10000 Hz) for 1 second duration (IKIN 4501-4516), four cycles were collected at low resolution (100 Hz) for 10 seconds (IKIN 4521-4528), and four cycles were collected at low resolution (100 Hz) for 20 seconds (IKIN 4531-4538). In all of the data acquisitions of this group, the programmable analog voltage input range of ± 1.2500 volts has been used. The higher input range than in some of the other fluoride ISE experiments was necessary because all of the cyanide electrograms showed larger voltage changes. The signal to noise ratio of the cyanide electrograms is sufficient to permit curves fitted to them using a nonlinear regression routine, however, these electrograms are of a lower quality than the fluoride (only) activity steps. Fitting a nonlinear curve could be done on these electrograms, but the curve fitting accuracy will be poorer due to the lower signal-to-noise ratio. The voltage resolution is less here than in the fluoride (only) steps, because of the larger voltage input range. As was the case with the hydroxide steps, digitization noise will be a significant source of error in any fitted curves. But like all of the experiments reported in this dissertation, the time resolution is still high, and the activity steps have been created extremely rapidly. Thus in these experiments fine details of the dynamic response to cyanide have been created and captured that may not have been seen using an instrument of lower time resolution or with an instrument that created slower activity steps. The majority, but not all, of the forward and reverse four-ion activity steps showed transient behavior. The non-monotonic forward steps showed rapid decreases in

voltage, followed by large, slow increases in voltage, approximating in shape an exponential curve. The non-monotonic reverse steps showed rapid increases in voltage, followed by large, slow decreases in voltage, the latter region again taking the form of an exponential curve. The exponential drift region of the reverse steps was particularly noisy. Some of the data collected for both the forward and reverse steps did not show the initial rapidly increasing or decreasing region, and showed only the uni-directional changes of the exponential region. The reason for this alternate behavior remains unclear at this time. Non-monotonic behavior in our previous experiments was the result of activity changes of hydroxide and/or static case non-interferent species. In the four-ion experiments all of these ions as well as cyanide are present, and thus non-monotonic behavior is not a surprising result, but the lack of it is. The reason for the lack of non-monotonic behavior may be linked to the constantly changing surface and near-surface regions of the lanthanum fluoride membrane. It is possible that if the time between the collection of a forward and reverse step cycle, or between a reverse step and the next forward step is too long, then such non-monotonic behavior may be missed altogether, because the surface of the lanthanum fluoride membrane has relaxed or otherwise changed in between the change in the solution flowed onto the membrane. Since chloride, bromide, and cyanide are not static case interferents, there is no selectivity coefficient reported for them in the literature. The step in hydroxide ion going from fluoride solution one to fluoride solution five is expected to cause a Nernstian change in voltage of -23.6 mV in a static case. The initial voltage change taking

place before the slowly drifting region in the forward steps exceeded the expected Nernstian value for the group as a whole. Files IKIN 4521-4528 will not be discussed, because files IKIN 4531-4538 show the same general behavior, but with a twice longer duration of sampling. In these activity steps, hydroxide, cyanide, chloride, and bromide have been stepped in their activities, as well as sodium, potassium, and nitrate. Hydroxide has been stepped from 1.0×10^{-6} M activity in fluoride solution one to 2.5×10^{-2} M activity in fluoride solution five. Cyanide has been stepped from zero activity in fluoride solution one to 3.0×10^{-3} M activity in fluoride solution five. Chloride and bromide have each been stepped from zero to 3.0×10^{-3} M activity. Sodium has been stepped from zero activity in fluoride solution one to 6.0×10^{-3} M activity in fluoride solution five. There is a minute and negligible change in the activity of potassium, decreasing for forward steps. The same can be said of the activity step of nitrate. As was explained in the chloride-bromide results, the possible effects of the step in sodium cannot necessarily be excluded in our four-ion results.

High (time) resolution forward four-ion activity steps. Figure 3-11 shows a very high time resolution (10000 Hz) forward four-ion activity step to represent the group of datum taken, and Figure 3-12 shows the companion reverse activity step. Figure 3-11 is a plot of the data of file IKIN 4501, while Figure 3-12 is a plot of the data of file IKIN 4502. The forward four-ion activity step shown in Figure 3-11 shows three main regions. Region one is a stable response to fluoride solution one and lasts for 10 milliseconds, these datum points being the 100 lead-in datum

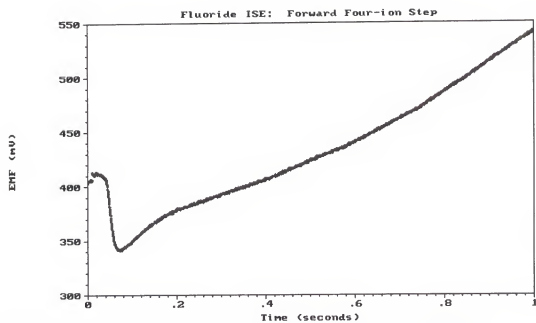


Figure 3-11. Forward four-ion activity step at very high resolution.

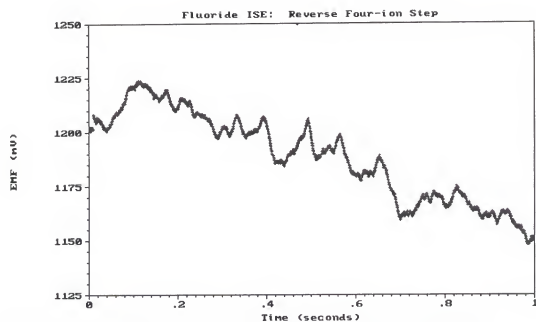


Figure 3-12. Reverse four-ion activity step at very high resolution.

points. Following region one there is the voltage spike. Region two begins when the electrode begins to respond swiftly to fluoride solution five. There is a decrease in the initial voltage by approximately 65 millivolts within 60 milliseconds after the change of solutions. Region three begins when there is a large and rapid drift towards higher voltages, and begins about 60 milliseconds after the change of solutions. The voltage never becomes stable in the first second of recorded data. The static selectivity coefficient for hydroxide in the fluoride ISE is 0.10.⁴² Fluoride solution five has hydroxide equal to 2.5×10^{-2} M activity, and so the equivalent fluoride activity of hydroxide is 2.5×10^{-3} M. Using the Nicolsky equation, the hydroxide's contribution to the voltage change is expected to be -23.6 millivolts. The measured change in voltage of the second region is about -65 millivolts, and is well beyond the Nernstian change in voltage expected from just the change in hydroxide ion activity alone. Comparing to the earlier hydroxide (only) steps (Figure 3-5), the second region of the forward four-ion step has decreased by about 65 millivolts and has a single minimum, while the second region of the forward hydroxide steps had two minima and each decreased about 30 millivolts. In the case of the earlier hydroxide (only) steps, the overshoot was due solely to hydroxide, while in the case of the four-ion steps, contributions to the minimum could be from both hydroxide and cyanide, with possible contributions from chloride, bromide, and/or sodium as well. The forward four-ion steps have a voltage overshoot about twice that of the hydroxide (only) steps, and for a step in hydroxide approximately one third of the hydroxide steps. It is tempting to attribute the

overshoot voltage in the group of the forward four-ion steps to the summation of the hydroxide steps (-24 millivolts if Nernstian) and the contribution of the concurrent chloride-bromide step (-27 millivolts) seen in Figure 3-9. If this were true, then we would have predicted a change in voltage of -51 millivolts compared to the measured -65 millivolts, the discrepancy perhaps within an acceptable estimation of the experimental uncertainty, but this explanation cannot hold true for the following reasons. First of all, the hydroxide (only) step did not give a Nernstian voltage change, but rather only -30 millivolts to the expected -51.5 millivolts, or only 58 percent of the expected Nernstian change in voltage. Thus we expect the hydroxide's contribution to the total change in voltage of the four-ion step to be much less than the Nernstian value. Secondly, the chloride and bromide steps in the case of the forward four-ion step were only two thirds as large as was the case for the chloride-bromide (only) step. Thus we would expect a contribution slightly less than that of the chloride-bromide (only) step. Finally, looking back at the forward chloride-bromide steps (Figure 3-9), we are reminded that while the forward chloride-bromide activity steps decreased about 27 millivolts, the time it took to complete this voltage change was about 700 milliseconds, a much longer time frame than either the forward hydroxide overshoot voltage or the forward four-ion overshoot voltage, which were completed within about 70 and 60 milliseconds respectively (Figures 3-5 and 3-11 respectively). Thus in the case of the forward four-ion activity steps, the effects of chloride, bromide, and sodium cannot contribute more than a few millivolts within the 60 milliseconds that the forward

four-ion overshoot voltage takes place within, due to the much slower rate of change of the chloride-bromide overshoot voltage. Thus the voltage change for the forward four-ion activity step (considering only the effects of hydroxide, chloride, bromide and sodium) should be in the range of less than a 30 millivolt voltage change in magnitude, which is still far short of the measured -65 millivolt change for that experiment. Another explanation must be sought to describe the larger than expected voltage change of the four-ion step. Since the effects of hydroxide, chloride, bromide, and sodium have been reasonably accounted for, this leaves only cyanide and hydrogen cyanide as the species that could be causing the larger than expected overshoot voltage in the four-ion activity steps. Thus it is clear that cyanide ion and/or hydrogen cyanide effect the magnitude of the overshoot voltage in the fluoride ISE, which is an unanticipated result. Further evidence can be seen by comparing the forward hydroxide overshoot voltage lineshape and the forward four-ion overshoot voltage lineshape within the first 400 milliseconds of collected data. The lineshapes of the hydroxide (only) overshoot voltages showed two minima, while the four-ion lineshapes showed only a single minimum. These qualitative differences in lineshape suggest the possibility of slightly different processes taking place in the reaction with the lanthanum fluoride of the fluoride ISE membrane, or a difference in kinetics, or could be the result of a lack of resolution of two (or more) minima. In a later section, it will be shown that the more probable cause is a lack of resolution of a double (or triple) minima, with differing chemical reactions and differing kinetics secondary possibilities.

High (time) resolution reverse four-ion activity steps. Figure 3-12 graphs the data of file IKIN 4502, the reverse four-ion step immediately following the data shown in Figure 3-11. Again, the reverse four-ion activity step shows three main regions. The first region is the region consisting of the 100 lead-in datum points, lasts for 10 milliseconds, and is a stable response to fluoride solution five. Then there is the voltage spike as the solutions are alternated. Soon afterwards, the electrode begins to respond to fluoride solution one. The voltage rises by approximately 23 millivolts within 110 milliseconds after the change of solutions. The third and final region begins about 160 milliseconds after the change in solutions, and is a large, noisy, and slow drift towards lower voltages. This drift never subsides within the first second of the electrogram. The voltage change of the second region reflects a change in voltage of a magnitude roughly what is expected due to the hydroxide (only) contribution to the voltage change. Thus it seems that the reverse step voltage changes are influenced primarily by hydroxide, unlike the forward four-ion steps which showed a considerable influence from cyanide. This too is a unforeseen result. Remembering that the reverse hydroxide step lineshape showed a very weak maximum at 60 milliseconds after the change in solutions followed by a much stronger maximum at 240 milliseconds after the activity step (Figure 3-6), it is entirely possible that in the four-ion reverse steps the first hydroxide maximum (if there is such a feature) may be below the limit of detection since a lower hydroxide activity has been used. The time that the second maximum in the reverse hydroxide (only) steps occurred was 240 milliseconds,

which is longer than the single maximum seen in Figure 3-12 by about a factor of two. However, reverse four-ion steps collected after more cycles showed a single maximum appearing at longer times, and the last few reverse steps taken showed a single maximum that appeared at roughly 200 milliseconds. The latter data show a maximum corresponding roughly to the second maxima of the hydroxide (only) steps for the time of appearance of the maximum. Because of this, it is possible for this behavior to be the effects of the alteration or dissolution of the lanthanum fluoride membrane upon repeated exposure to the hydroxide and cyanide containing fluoride solution five, but further comments beyond this are speculation. Clarification of this could be obtained by a series of experiments involving a repeated exposure of the lanthanum fluoride membrane to fluoride solution five, combined with surface analysis via X-ray Photoelectron Spectroscopy. This experiment would best be performed using an ISE for which the membrane can be removed for surface analysis, but replaced for electrochemical analysis. Such a removable-membrane ISE has been made in our laboratory for this type of experimentation, and the preliminary results obtained show the merit of such an arrangement. It is engrossing to find that while cyanide has effected the forward four-ion steps, it has had little effect, if any, on the reverse four-ion activity steps. The reason for this may be based in the kinetics of the reaction(s) taking place, or the reactions involved in the forward and reverse steps may be largely chemically irreversible. Chemical analysis of the surface region of the lanthanum fluoride membrane by X-ray Photoelectron Spectroscopy ⁵⁸ could determine if the surface

of the lanthanum fluoride membrane is altered upon exposure to cyanide, and if this surface can be regenerated by means of soaking in a fluoride containing solution. The exact reaction(s) taking place and their possible mechanism cannot be stated in a preliminary study of the effects of cyanide such as the experiments reported here. The reverse four-ion step overshoot response time is 110 milliseconds, and is about twice that of the forward step, which follows the trends seen in both the previous experiments reported in this dissertation and by other researchers.^{1,2,36,51,52}

Low (time) resolution forward four-ion activity steps. Figures 3-13 and 3-14 exhibit the fluoride ISE response following a forward (Figure 3-13) and reverse (Figure 3-14) activity step using fluoride solutions one and five, but with a low sampling rate (100 Hz), and for a duration of sampling of 20 seconds. The forward four-ion activity step data file shown in Figure 3-13 is IKIN 4533, and its companion reverse activity step shown in Figure 3-14 is IKIN 4534. Here the activity step is created after 1 second of measuring the voltage response to fluoride solution one, because the sampling rate is 100 Hz, and 100 lead-in datum points require 1 second to acquire. The same common behavior shown in the other forward four-ion step is seen in this figure also, but the drift region is more fully revealed. In Figure 3-13 the voltage spike cannot be seen because of the low sampling rate, which illustrates the superiority of an instrument capable of creating very rapid activity steps and capturing fine details with very high time resolution. After the activity step the voltage decreases sharply by about 67 millivolts, again reflecting a change of voltage of a much larger magnitude than that expected by the Nicolsky equation if

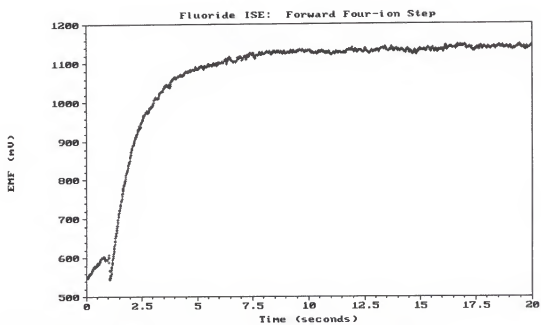


Figure 3-13. Forward four-ion activity step at low resolution.

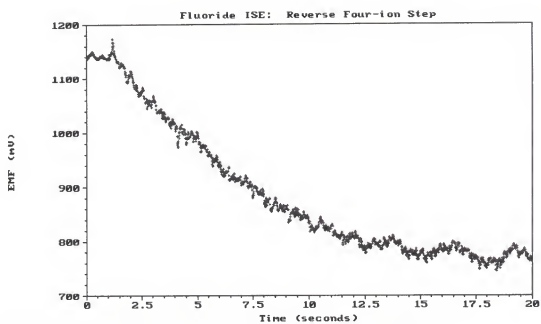


Figure 3-14. Reverse four-ion activity step at low resolution.

based solely on hydroxide (-23.6 mV). A slow voltage drift towards higher voltages of about 590 millivolts occurs, which appears to stabilize around 14 seconds after the exchange of solutions. The drift region seems to follow an exponential lineshape. No additional features are seen in this figure upon comparison to Figure 3-11, except that the slowly drifting region can be seen to stabilize. The same conclusions as were made with the high (time) resolution forward four-ion activity step can be made with the low (time) resolution four-ion activity step.

Low (time) resolution reverse four-ion activity steps. In Figure 3-14, a representative low (time) resolution reverse four-ion activity step is shown, in this case the reverse step immediately following the data shown in Figure 3-13. The low (time) resolution reverse four-ion step shows the same three regions as the high (time) resolution reverse four-ion step. First a noisy initial voltage for the electrode responding to fluoride solution five lasts for 1 second. The solutions are then switched. Here too the voltage spike cannot be seen due to the low sampling rate. Then a voltage increase of about 35 millivolts occurs. This voltage change is of a larger magnitude than the 23.6 millivolts predicted by the Nicolsky equation, which can only consider the effects of hydroxide ion. The measured voltage change also reflects a voltage change that is larger than the estimated voltage change, which was said to be less than 30 millivolts. However the actual voltage change is only very slightly larger than the estimate. The measured voltage change is also larger than the voltage change in the high (time) resolution reverse four-ion activity step. Lastly, a slow, noisy drift to lower voltages occurs. The drift is about 380 millivolts

towards lower voltages, and seems to be close to reaching an equilibrium value at the end of the sampling period. Again, it seems that the drift region could be fitted by an exponential curve.

Comparison of forward and reverse four-ion activity steps. Upon comparison of Figure 3-11 to Figure 3-12, it is apparent that the kinetics are faster for the forward four-ion overshoot voltage change than for the reverse, due to the longer overshoot response times in the reverse activity step, which follows the behavior of the monotonic voltage changes of the fluoride steps reported earlier. Upon comparing Figure 3-13 with Figure 3-14, the kinetics of the drift region are also faster for the forward four-ion step than the reverse step. This follows the trend of the results of the hydroxide steps given earlier. The voltage change of the overshoot leading to the voltage minimum for the forward four-ion step (-65 millivolts) is much larger in magnitude than the change in voltage leading to the voltage maximum in the reverse four-ion activity step (23 millivolts). In the case of the forward steps, there is strong evidence of cyanide species contributing to this voltage change. In the case of the reverse steps, cyanide species have had little or no effect on the overshoot voltage change. This indicates that the reactions with regard to cyanide in the fluoride ISE are chemically irreversible or have vastly differing kinetic rates, just as the reactions with regard to hydroxide were shown to be at least partially irreversible. However, the symmetry of the lineshapes of the forward and reverse four-ion steps shows that at least some of the reactions in the four-ion steps are chemically reversible and of a similar time-frame. The voltage

change during the drift region is larger for the forward step than the reverse step, and by about 200 millivolts. The reasons for this and the implications that this result has are not clear at this time. The reason for this discrepancy in the response time of the forward and reverse overshoot voltages in the case of the four-ion steps could be due to different reactions between the cyanide species and the lanthanum fluoride membrane or different kinetic rates for the forward and reverse reactions, or due to the lack of resolution of a double minima and maxima as is elaborated in the next section.

Comparison of four-ion activity steps to hydroxide activity steps. In both the four-ion steps and the hydroxide (only) steps, a step in hydroxide has been performed. In the case of the hydroxide (only) steps, the activity step in hydroxide was larger than for the four-ion steps, and in the case of the four-ion steps, there is a concurrent step in cyanide. In the hydroxide (only) steps, there were two minima or maxima seen in the voltage overshoot. For forward hydroxide (only) steps the minima occurred at 41 and 66 milliseconds on the average, and for reverse steps the maxima occurred at 59 and 230 milliseconds. For the first few hydroxide (only) cycles, the overshoot voltages were small in the forward steps and large in the reverse steps. Later hydroxide cycles showed a decrease in the magnitude of the forward overshoot voltage changes and an increase in the magnitude of the reverse overshoot voltage changes. This was attributed to chemical irreversibility towards hydroxide or a large difference in the rate of reaction towards hydroxide. In the case of the four-ion steps, cyanide was shown to have

an effect on the forward steps, but little or no effect on the reverse steps. There is but one minimum or maximum seen in the four-ion steps, probably due to the lack of resolution of a double minimum or maximum, but this also could be due to different reactions with the surface of the lanthanum fluoride membrane of the fluoride ISE. The minimum of the forward four-ion steps typically occurred at about 62 milliseconds, the range being 50 to 80 milliseconds, and the maximum of the reverse steps typically occurred at about 158 milliseconds, the range being 100 to 220 milliseconds. The forward four-ion minimum corresponds roughly to the time of the first or second minima of the hydroxide (only) steps. Again it may be possible that only one minimum is seen because of the lack of resolution of the two minima seen in the hydroxide (only) steps, or it could be because of different chemical reactions taking place or a difference in kinetics. In the case of the reverse steps, the maximum seen in the four-ion steps begins to appear at a time somewhere in between the two maxima seen in the hydroxide (only) steps, and in later steps it appears at a time closer to the second maxima seen in the hydroxide (only) steps, which is evidence to support the lack of resolution of a double maxima, or differing chemical reactions.

Conclusions

There were two main reasons for doing this research. First of all, it was contracted to us for development of the Hoke analyzer. Secondly, it is basic research into the effects of interferents on the dynamic response of ion-selective

electrodes, which is a subject which has not been investigated much before our efforts. The rates of response to primary and interferent ions in ISE dynamic response need not necessarily be the same, so this question is also important when analyzing complex mixtures of salts in flowing streams of analyte solution. We have analyzed solutions whose chemical content simulates fuel and ammunition fires in armored fighting vehicles having been extinguished by Halon fire extinguishers. The Hoke analyzer in its fully developed form would be able to measure the hydrogen halide content of the post fire environment of these fuel and ammunition fires, also known as "brew ups." While we have investigated other halide electrodes and solutions, this dissertation concentrated on the converging wall-jet instrument and our experiments with the fluoride ISE. In the case of fluoride steps, the response is rapid, Nernstian, reversible, and with moderate voltage drift. The forward response times were shorter than the reverse response times, which followed similar studies of forward and reverse steps for other researchers. In the case of the hydroxide steps, the only reported interferent for the fluoride ISE, we see non-monotonic behavior in both the forward and reverse steps, the voltage responses were rapid, sub-Nernstian, not completely reversible within the time frame of the experiment, and showed extreme voltage drift. Surprisingly, our experiments with chloride/bromide steps showed a moderate dynamic response in the forward direction and a weaker response in the reverse direction. The voltage responses here were much slower than the fluoride or hydroxide responses, and also were non-monotonic. They were not completely reversible within the time

frame of the experiment, and exhibited slight voltage drift. The response to chloride/bromide steps illustrates that species that give no response in the static case may give dynamic responses. It also illustrates that an ISE may have different response times to different ions, such as the case here where the fluoride ISE has responded to fluoride and hydroxide much faster than to chloride/bromide. In the case of our four-ion experiments, we report that while cyanide is not a static case interferent, we have inferred that a dynamic response towards increasing steps in cyanide results. The response time is about the same as fluoride or hydroxide steps. This response was weak in the forward direction, and in the reverse direction the response due to cyanide was either extremely weak or there was no response. Thus in the case of the fluoride ISE, many species can give a dynamic response, while in the static case only fluoride and hydroxide are known to give voltage responses.

CHAPTER 4 FUTURE WORK

Correlation of the Surface State of Ion-selective Electrodes to Their Dynamic Response

Design of a Demountable Membrane Ion-selective Electrode Body for Correlated Dynamic Response and Surface Studies

This dissertation has presented studies of the dynamic response of ion-selective electrodes, but our research efforts have also been directed at studies of their surface composition.^{59,60} It is likely that the surface composition and/or surface morphology could influence the dynamic response of ion-selective electrodes, making them respond faster or slower following rapid changes in primary or interferent ion activities. For example, a chloride ISE that has been poorly maintained may have a roughened surface compared to a new electrode. This factor may cause a measurable effect on the dynamic response of the electrode. It may be explored by means of experiments correlating electron microscopy and profilometry measurements with dynamic response measurements obtained using the converging wall-jet instrument. For dynamic response measurements, one must have a functional, complete ISE. For electron microscopy

and profilometry, one can examine only the ISE membrane and not the ISE membrane/electrode body assembly.

A demountable membrane ion-selective electrode body. To do the proposed experiments one needs to have an electrode body for which the membranes can be mounted for dynamic response measurements and demounted for electron microscopy and profilometry studies. The literature does contain descriptions of ISE bodies which have removable membranes.^{61,62} There are also several studies of the dynamic response of ISEs using advanced instrumentation.^{6,10,11} There have been many electron microscopy studies of the surfaces of ISE membranes.^{63,64} To date, no studies have appeared in the literature on the dynamic response of ISEs using a demountable membrane ISE body. Such a demountable membrane ISE body for dynamic response studies can be made. It shall differ from a regular ISE body in the following ways. It shall have a screw cap to hold the membrane against the electrode body. It shall also use "O-rings" for sealing the junctions of the screw cap with the membrane and the membrane with the electrode body. It will require a stainless steel disk behind the membrane for electrical continuity. This disk will have a coupling to the coaxial cable of the ISE. No further modifications are envisioned to make a functional ISE for the proposed experiments.

Procedure for studying the effect of surface roughness. Using the previous example of the chloride ISE, the experiment would require the following basic steps. First the electrode would be assembled and the dynamic response of a new membrane would be measured. The membrane would be removed and examined

by profilometry. This technique allows linescans to be made of the surface morphology. The resulting waveforms can be analyzed by harmonic analysis to provide quantitative measures which are directly related to surface roughness. Alternatively, an average amplitude and average frequency can be determined for a "one wave" approximation.⁶⁵ The membrane would also be examined with electron microscopy. The electrode membrane would be roughened with sandpaper or by chemical etching and then assembled into the electrode body. Its dynamic response would be measured for the second time. The membrane would be demounted and subjected to profilometry and microscopic examination for the second time. The membrane will be polished smooth again and remounted in the electrode body and the dynamic response measured again. Lastly, the surface state will be examined for the third time with profilometry and electron microscopy. A complete study will have been accomplished and a conclusion about the correlation (or lack thereof) of dynamic response to surface roughness can be drawn.

The Effect of Bromide Contamination on the Dynamic Response of the Chloride Ion-selective Electrode

The dynamic response of a chloride ion-selective electrode contaminated with bromide correlated to its surface composition. This experiment would look at the effect that a changing surface composition would have, if any, upon the rate at which an ion-selective electrode can respond. The electrode used would be a chloride ISE, which contains silver chloride in its membrane. First the XPS spectra

of a new membrane would be taken, with particular emphasis placed on the Cl2p/Br3p, Ag3d, O1s, and C1s regions. The rate of electrode response would be measured for a new membrane in the demountable membrane ISE body. The electrode membrane would then be demounted, XPS measurements of the surface taken, and then soaked in a bromide containing solution. From previous efforts we know that the bromide will replace some of the chloride at the surface of the membrane, due to the lower solubility of silver bromide. The electrode will then be mounted again and its electrochemical response measured. Now that the surface has become a mixture of silver chloride and silver bromide, this may effect the rate of electrochemical response of the electrode. The experiment just described will reveal if there is a change in the rate of electrode response as ion exchange processes change the surface of the electrode membrane. To our knowledge, no previous experiments comparing ISE dynamic response to surface composition have appeared in the literature. We believe that a measurable change in the electrode response is likely when the surface becomes substantially contaminated with bromide. A series of XPS measurements and dynamic response measurements will be taken of the chloride ISE membrane after each of several periods of exposure to the bromide containing solution.

The dynamic response hysteresis experiment for bromide contamination on a chloride ion-selective electrode. After exposure sufficient to cause a considerable replacement of bromide for chloride, a hysteresis experiment will be performed. From previous efforts in our lab we know that the bromide contamination can be

removed with exposure to 0.1 M HCl. It would make a very interesting experiment to record the change in dynamic response of the bromide contaminated chloride ISE as the surface composition is brought back closer to its initial composition. It is of practical value to see if it is possible after considerable contamination has taken place for a solid state ISE's dynamic response to be brought back to the level of performance of new electrodes.

The Effect of Cyanide Species on the Dynamic Response of the Fluoride Ion-selective Electrode

This study would follow the same general methodology of the previous experiment including the demountable membrane ISE body, but would use a fluoride ISE and a cyanide solution as the contaminant. We have seen in Chapter 3 of this dissertation that the fluoride electrode showed a dynamic response when exposed to cyanide as an interferent. This is a surprising result, as cyanide had not been reported as an interferent for the fluoride electrode. An XPS investigation of the changes of the surface of the electrode membrane as it becomes exposed to cyanide is warranted. The fluoride electrode studied was made from lanthanum fluoride, LaF_3 . Since cyanide ion or solvated hydrogen cyanide is causing an unexpected electrode response, it would be interesting to look at what surface species of cyanide (if any) exist. However, if one has a demountable membrane ISE body and a converging wall-jet instrument, then one can do the XPS and dynamic response experiments using the same membrane and determine if the

change in the surface state is responsible for the changes in the rate of electrode response. This experiment would follow the method of the previously mentioned experiment involving the bromide contamination of the chloride electrode.

Measurement of the Dynamic Response of the Lead Ion-selective Electrode and Correlation to Light-induced Corrosion

Preparation of lead ion-selective electrode membranes excluded from oxygen and light. The lead ISE has been a subject of interest in our lab.^{59,60} The membrane composition for the lead ISE is often a 50/50 molar ratio of lead sulfide and silver sulfide. We have shown previously using XPS that the corrosion of the lead ISE membranes is enhanced by white light.^{59,60} The oxidation of sulfide in the samples to sulfate was seen. We had prepared fresh co-precipitate powders of lead sulfide and silver sulfide in a special light-tight synthesis box, then purified and pelletized the powders. Some samples were prepared such that exposure to room lighting occurred. Aging of the pellets was accomplished in light and in darkness. We learned that the membranes, despite our best efforts, contained significant oxidation products for freshly prepared samples.^{59,60} For additional work with these membranes, a more satisfactory method of making the samples was found to be desirable to improve on their freedom from corrosion products. A more satisfactory purification and drying procedure resulted in the production of samples that showed no signs of sulfate corrosion,⁶⁶ and decreased sulfur corrosion⁶⁶ compared to our earlier efforts.^{59,60} The setup used to make the samples has been described previously.^{59,60,66} By performing a sample synthesis with the enhanced preparation,

purification, and pelletization steps, the freshly prepared pellets will be largely corrosion free, and excellent samples for this experiment.

Effect of oxidative corrosion as catalyzed by light on the dynamic response of the lead ion-selective electrode. Much like the previous examples of correlated studies of surface composition and dynamic response upon sample contamination, the effect of light-catalyzed oxidation of a lead ISE membrane on its dynamic response could be studied. The studies of the changes in surface composition upon oxidation in light and in darkness have been done in our lab previously.^{59,60} The surface composition of the samples will be revealed by XPS, and a general method similar to that proposed for the chloride contamination study be used. Again, the demountable membrane ISE body will be used for dynamic response measurements in between XPS analyses. A freshly prepared pellet will be analyzed with XPS and its dynamic response measured. The dynamic response of the lead ISE has not yet emerged in the literature, making this in and of itself a measure of progress. The sample will then be aged by exposure to room lighting and air, which we have previously seen will cause oxidation of the surface of the sample.^{59,60} The XPS analysis will be repeated, thus confirming the extent of oxidation, and the sample will be remounted in the demountable membrane ISE body for subsequent dynamic response measurements. It is likely that the dynamic response will now be slower. The cycle of sample exposure to light and air, XPS analysis, and dynamic response measurements will be repeated until the sample is heavily corroded, ceases to show any response, or both. The effect of corrosion on ISE

dynamic response will have been detailed for the first time. An additional experiment can be done for the lead ISE, namely the effect of light itself on the dynamic response. Light injects electron-hole pairs into the semiconducting lead sulfide, which has a band gap of 0.41 eV.⁶⁷ The additional conductivity due to these electron-hole pairs could effect the dynamic response of the electrode. A simple experiment can be done where a freshly prepared membrane is mounted in the demountable membrane ISE body. The dynamic response will be measured as the converging wall-jet instrument is shielded from room lighting. Then the experiment will be repeated with the lead ISE being exposed to full room lighting. Next, additional light from an incandescent lamp will be shown on the membrane of the lead ISE and its dynamic response recorded. Finally a check of the hysteresis on the dynamic response of the lead ISE upon exposure to different lighting levels will be shown by repeating the experiment with the membrane again shielded from room lighting. The effect of light on the dynamic response of the lead ISE will have been shown for the first time.

The Dynamic Response of the Fluoride Ion-selective Electrode to Halide and Cyanide Ion Activity Steps

The results of our preliminary experiments on the fluoride ISE shown in Chapter 3 revealed unexpected results, and will need to be repeated in part for more clarity on the effects of the various individual ions studied. Chloride and/or bromide ion had an effect on the dynamic response, an unexpected result. Due to

the manner in which the experiment was performed, it could not be said whether each ion had an effect or whether only one ion caused the dynamic response. If it was a solitary ion, it was not determined which ion caused the effect. A repeat of this experiment to clarify the earlier results will be necessary. Also, it was deduced that cyanide had an effect on the dynamic response of the fluoride ISE, but the solution used contained concurrent steps in chloride, bromide, and hydroxide. To prove the response to cyanide, an experiment with a step in cyanide alone should be performed for the fluoride ISE.

The Effect of Chloride Ion Activity Steps

It was shown in Chapter 3 that chloride and/or bromide caused a dynamic response for the fluoride electrode. The extent of each individual ion's responsibility for the dynamic response noted could not be determined. If this experiment were repeated with chloride ion being the only interferent ion present, then the effect of chloride ion can be unequivocally demonstrated.

The Effect of Bromide Ion Activity Steps

As per the previous paragraph, more clarity is needed for the effects of the bromide ion on the fluoride ISE. This experiment will also need to be repeated, with solutions being made containing bromide ion as the only interferent. If this is done, then the extent of dynamic response due to the bromide ion can be shown.

The Effect of Cyanide Ion Activity Steps

The final repetition of the fluoride ISE experiments will be to reveal the exact nature of the function and extent of the effect of the fluoride ISE's dynamic response towards cyanide species. The efforts reported in Chapter 3 showed that a dynamic response towards cyanide ion was probable. The complexity of the solution used for this experiment prohibited a statement of the extent of the dynamic response or the line shape of the dynamic response of the fluoride ISE to cyanide ion or hydrogen cyanide. A follow up study with cyanide as the only interferent will reveal both of the sought after experimental results. This experiment will require a solution of low or neutral pH to minimize the effects of hydroxide ion. At the same time, a high pH is desired to reduce the levels of toxic hydrogen cyanide liberated. One cannot satisfy both conditions, so a neutral pH seems to hold the promise of leading to a workable compromise that should lead to the desired results.

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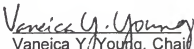
BIOGRAPHICAL SKETCH

Michael Louis Clay was born in Galesburg, Illinois, on October 9th, 1962. In 1980 Michael graduated from Galesburg High School, with his academic standing in the top 10 of his class of about 500 students. He received many prizes and awards related to scholastics and his studies of the sciences. It was at this time that he began to develop a strong interest in science, with chemistry as his favorite subject. He developed a special interest in chemical analysis instrumentation by doing an independent study with an ultraviolet-visible spectrometer.

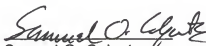
Michael continued his education at Knox College in Galesburg, Illinois. In 1984 he graduated from Knox College with the degree of Bachelor of Arts, with chemistry being his major field of study.

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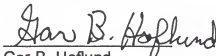
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1996

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